Correlations for the prediction of higher heating values of liquid fuels from their densities, viscosities, and flash points values

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Abstract
In this study, correlations of the higher heating values (HHV) of three groups of liquid fuels, vegetable oils, alkanes, and alcohols were developed through experimentation and prediction with the aid of the statistical software package MINITAB 16 (PA, USA). The HHVs (in kJ/kg), of the samples were obtained as a function of the density, viscosity, and flash points physical tests. Reliability of models were evaluated through statistical validation and cross-validation standard error of estimate (S), coefficient of determination (R^2), predicted residual error of the sum of square statistics (PRESS statistics), error estimations (average bias error, ABE, and AAE, average absolute error), and the residual versus fitted values plot. For the vegetable oils, the best correlation was HHV = -29.5 + 77.8ρ -0.0124μ + 0.00549β (R^2 = 79.6%, *p*-value = 0.147, AAE = 0.515, ABE = 0.005). For alkanes it was: HHV = 66.0322 – 38.3421ρ + 2.9392μ (R^2 = 100%, *p*-value = 0.002, AAE = 0.033, ABE = 7.27 x 10^{-5}). For alcohols; HHV = -100 + 171ρ (R^2 = 86.4%, *p*-value = 0.070, AAE = 4.193, ABE = 0.316). These correlations could be instrumental to achieving maximum productivity with minimal utilization of energy in industry and could be extended to other liquid fuels after minor modification.

Keywords: Higher heating value (HHV), Isothermal bomb calorimeter, Average absolute error, Combustion, Regression analysis

1. Introduction
Higher heating value (HHV) defines the quantitative energy content of fuels (solid, liquid, or gas) and relates to the clean and effective use of these fuels [1,2]. The most imperative properties of fuels that gives explanation to the higher energy content and determine the efficient application of liquid fuels is HHV. Furthermore, the higher heating values , HHVs comprise the latent heat of the water vapor products of combustion for the reason that the water vapor is allowed to condense to liquid water [3]. Higher heating value also assists in understanding the quality of a fuel [4]. HHV is often represented with a unit of energy or heat per unit mass. It is the amount of heat or energy released when a gram of the fuel is burnt to give carbon dioxide and water at a prevailing temperature and pressure [5]. Energy generation systems often require strong approach in evaluating or predicting crucial fuel characteristics. Issues that are presently facing three critical problems in association to fuels can be grouped into four; high fuel prices, climatic changes, air pollution, and heating value [3]. Heating values affect transporting and storage of fuels, just as the temperature at flash point [6]. If the heating value is high, small fuel storage tanks can be transported over long distances. High heating values also favour higher power output from smaller engines [6]. Fuel properties can be determined using expensive devices, which add to the cost of the energy process. Most common experimental methods of

evaluating heating values of fuels are through proximate, ultimate, and chemical analyses [5]. However, these methods are based on special instruments that are expensive. Therefore, because of high costs of analysis, simple and cost-effective methods of estimating fuels characteristics are needed [5,6]. Studies between HHV and some fuel properties were previously reported [7,8,9].

In this study, two approaches (experimentation and prediction) were used to obtain mathematical relationships for estimating the HHV of three liquid fuels (vegetable oils, alkanes, alcohols). Data generated from the measurements of the density, viscosity, and flash points of the liquid fuels were used to develop the correlations between the higher heating values and measured values using linear regression method. Furthermore, for reliability of developed relationships, statistical validation and cross-validation were carried out using dependable parameters such as standard error of estimate, S, coefficient of determination, R2, predicted residual error of the sum of square statistics, PRESS, error estimations (average bias error, ABE, and AAE, average absolute error), and the residual versus fitted values plot.

2. Experimental Methods

2.1. Materials

The vegetable oils were obtained from the local oil producers in Ogba area of Lagos State, Nigeria. The vegetable oils were filtered to remove suspended solid particles that can adversely affect the analyses as described elsewhere [10]. The alkanes and alcohols were of laboratory analytical grades.

2.2. Quality Parameter determination

2.2.1. Higher heating value

The higher heating value (HHV) of the liquid fuels was determined with an isothermal oxygen bomb calorimeter (DIN 51900-3) method [11]. A total weight of 1 g of the material was positioned in a crucible and inserted into the bomb. The design of the bomb was done for the purpose of withstanding pressure and heat using a large flask in order to hold the bomb with an identified volume of water. The bomb was filled with oxygen (purity 99.99%) after closing it under the pressure of 2,020 kPa. The bomb was then positioned in the adiabatic calorimetric apparatus filled with water and the sample electrically kindled by means of using a fuse wire [12]. The progression of the process increases water temperature allowing for the calculation of HHV of the material [13]. Benzoic acid was used as the reference substance for standardization. The heating value of a sample was obtained through the heat generated per unit weight of the material. The standard heating value of benzoic acid was determined with its identified combustion of heat and subsequently utilized for the determination of the bomb calorimeter heat capacity [12, 13]. Figure 1 shows the temperature profiles for the different vegetable oils during the heating process.

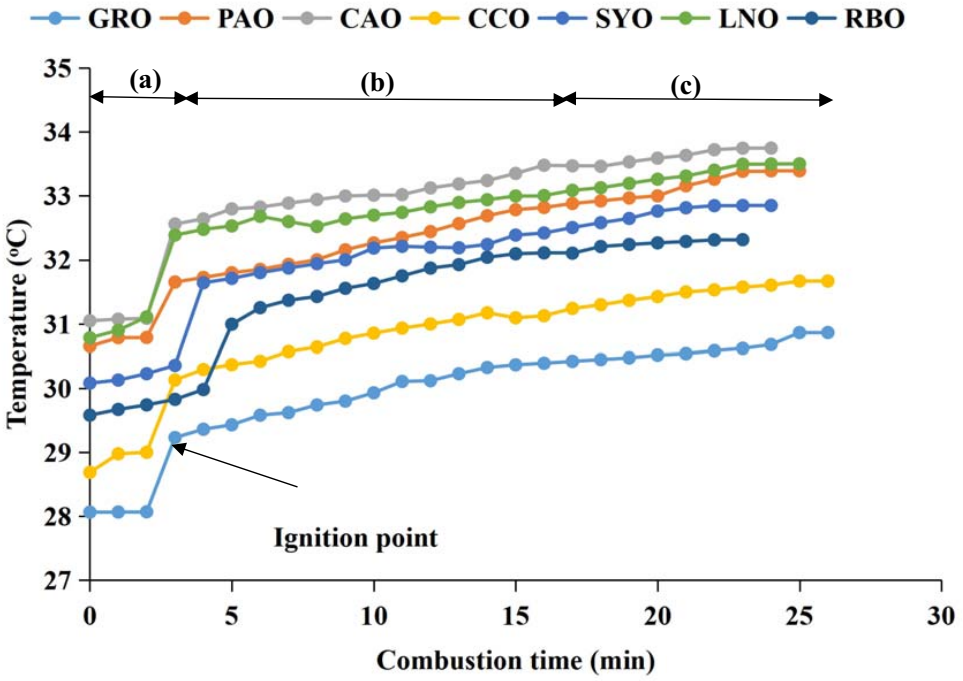


Figure 1**:** Temperature rise in the bomb calorimeter during the combustion of vegetable oils, GRO = groundnut oil, PAO = palm oil, CAO = castor oil, CCO = coconut oil, SYO = soya bean oil, LNO = linseed oil, RBO = rubber seed oil. Sections (a) temperature test period; (b) temperature rise period; (c) final temperature rise period.

2.3. Viscosity, flash point, and density measurements

2.3.1. Viscosity

It is an expression of resistance to flow and thus influences the flow of fuel through pipes and other equipment. It is dependent on temperature. Viscosity is the major factor in the storage and usage of fuel oil. It affects the degree of pre-heating for handling, storage, and atomization. If the oil is highly viscous, there becomes a difficulty in the ignition and operation of the burner. The apparatus used for the viscosity test is the 8-speed rotor viscometer. In this experiment, 350 ml of each liquid fuel sample was added to a stainless steel cup. The sample cup holder on the instrument was adjusted to submerge the rotor sleeve into the fuel samples at 28 ^{o}C. The temperatures used were 40 ^{o}C at rotor speeds of 600 rpm.

2.3.2. Flash point

It gives an indication of the flammability of the fuel. . It is the least temperature at which a product releases sufficient vapor to form an inflammable mixture with air under standard condition. Its significance is in the safety aspects of storing and handling the fuel. The liquid fuels were poured into the test cup to the filling mark. The test cup was then placed in the flash point tester. A thermometer was attached to the flash point tester and lowered into the test cup. Heat was applied to the base of the cup and the flame was ignited. At a particular temperature

(flash point), the flame was ignited and passed across the center of the cup until a flame temporarily propagates across the surface of the oil.

2.3.3. Density
It is the mass of a fuel divided by its volume at a reference temperature. It is measured with the use of a hydrometer. The density of a fuel helps us in calculating the calorific value of the fuel and gives an information of its ignition quality. Its unit is g/cm^3. A dried, clean 50ml capacity density bottle was weighed and recorded. The bottle was filled with the various liquid fuels and the weight was recorded. The mass of the fuels were obtained by subtracting the weight of the empty bottle from the weight of the bottle when filled with the liquid fuel. Data used in this study were average values of duplicated experiments.

2.4. Formulation of the predictive models

With the aid of the statistical software, MINITAB 16, predictive models were developed using regression analysis. In addition, the software was used in the statistical interpretation and validation of the developed correlations. The determination of the best fitting regression model was done through stepwise selection procedure. The governing equation can be described as follows:

$$Y = a_0 + a_1 X_1 + a_2 X_2 + \ldots a_k X_k + E \quad (1)$$

Y is the dependent variable of higher heating values
$a_0, a_1 \ldots a_k$ are the regression coefficients.
$X_1, X_1, \ldots X_k$ are the selected independent variables of density, viscosity, and flash point.
The regression models relate the higher heating values to density, viscosity, and flash point as the case may be. The measured values of the density, viscosity, flash point, and HHV of the three groups of liquid fuels are given in Table 1.

Table 1: Samples sets of vegetable oils, alkanes, and flash points with measured and calculated parameters

Fuel	Chemical formula	Density at 15 ^{o}C in g/cm^3	Viscosity (mPa.s)at 40 ^{o}C	Flash point ^{o}C	Experimental HHV (kJ/kg)	Calculated HHV (kJ/kg)
Vegetable Oil						
Groundnut oil	$C_{30}H_{45}N_9O_5$	0.884	40.5	270.00	37,037	37,026
Palm oil	$C_{16}H_{32}O_2$	0.882	135.0	186.00	36,226	36,248
Castor oil	$C_{57}H_{104}O_9$	0.958	338.0	180.00	39,699	39,670
Coconut oil	$C_4H_8N_9O_2$	0.898	37.0	280.00	37,021	38,093
Soybean oil	$C_{57}H_{98}O_{12}$	0.874	29.35	290.00	36,623	36,257
Linseed oil	$C_{57}H_{98}O_6$	0.901	30.0	215.00	39,960	38,835

Rubber seed oil*		0.890	29.50	120.00	38,159	38,603
Alkanes						
Hexane	C_6H_{14}	0.628	1.6	ND	46,655	46,656
Octane	C_8H_{18}	0.668	2.0	ND	46,297	46,298
Xylene	C_8H_{10}	0.826	1.8	ND	39,452	39,640
Toluene	C_7H_8	0.842	1.8	ND	39,015	39,086
Methanol	CH_3OH	0.720	1.7	ND	22,440	24,766
Ethanol	C_2H_5OH	0.764	2.0	ND	27,740	27,056
Propan-2-ol	C_3H_8O	0.760	2.1	ND	31,720	28,847
Butanol	$C_4H_{10}O$	0.788	2.8	ND	34,328	35,559

2.5. Estimation of the errors from developed models

The error of estimation terms, AAE (accounts for how close is the experimental or the observed response value of HHV to the predicted value)(Equation 2) and ABE (mathematically determines the amount of how high or low the correlations are)(Equation 3) [14,15].

$$AAE = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{HHV_{predicted}-HHV_{measured}}{HHV_{measured}}\right| x\ 100\% \quad (2)$$

$$ABE = \frac{1}{n}\sum_{i=1}^{n}\left[\frac{HHV_{predicted}-HHV_{measured}}{HHV_{measured}}\right] x\ 100\% \quad (3)$$

Small bias of the correlation corresponds to lower values of average absolute error and average bias error. A positive ABE indicates that the mean of the predicted value is greater than the observed value. Standard error of the estimate, S, gives the standard deviation associated with the error of prediction. The smaller the S value, the better the ability of the dependent variable to accurately predict the regression line. In other words, S is the mean position the observed value is away from the regression line. Therefore, a very small S reveals that the observations are closer to the regression line. The regression coefficient, R^2, shows the quality of the straight-line correlation. A high regression coefficient indicates that predictor variables are highly correlated. The high value of R^2 confirms how accurate and suitable the prediction model. The closer the R^2 to unity the better the correlation [16]. The predicted residual error sum of squares, PRESS, is a

cross-validation parameter measuring the model fit to a sample of observation that were not included in estimating the model. The smaller the PRESS statistic value the better the predictive ability of the regression model.
Statistical evaluations are not wholly restricted to validating regression models by number value parameters such as AAE, ABE, S, R^2, and PRESS statistics values, because it is difficult to adequately satisfy the conditions with only numbers. Comparison can also be done with plots such as residuals versus fitted value plot. The residuals account for the variation in the experimental to the predicted data while fitted values are important to show accuracy if the model fits to data. Therefore, a highly predictive model must show random pattern of residuals on both sides of zero for the residual versus fitted values plot. Accurate validity of model means that the residuals must be centrally located to the zero line throughout the range of fitted values [16]. If positive residuals control the plot or negative residuals control, then the error is not random. Such situation means that the predictors of the model are not explaining necessary information for the correlation [16]. In order to determine the performances of the developed correlations in this study, selected models were those with accurate predictions possessing precise residuals versus fitted values symmetry, highest regression coefficient, R^2, lowest values of S, PRESS statistic, AAE, and ABE.

3. Results and discussion

The mean values of the independent variables (density, viscosity, and flash points) of the fifteen liquid fuel samples with their corresponding experimental and predicted HHV values are given in Table 1. The density values of vegetable oils, alkanes, and alcohols varied between 0.882–0.958 g/cm^3, 0.628–0.842 g/cm^3, and 0.720–0.788 g/cm^3 respectively. The viscosity values for vegetable oils varied from 29.35–338 mPa.s, alkanes from 1.6–2.0 mPa.s, alcohols from 0.720–0.788 mPa.s (Figures 2 to 4). The flash point values varying from 120–290 ^{o}C were only evaluated for vegetable oils. The experimental HHV values ranged from the lowest for the liquid fuels, 22,440 kJ/kg (methanol) to as high as 46,655 kJ/kg (hexane). The HHV values closely agree with similar fuels as reported in the literature [5].

3.1. Effect of density, viscosity, and flash point values on HHV

From the experimental values of density, viscosity, and flash points of the vegetable oils, alkanes, and the alcohols (Table 1), correlations of HHV with individual and the combinations of the independent variables were developed through regression analysis (Equations 4 to 14).

Table 2: Statistical parameters for liquid fuels correlations for the prediction of higher heating value from the density, viscosity, and flash point values

	Correlation	R^2	S (kJ/kg)	PRESS (kJ/kg)	*P*-value	AAE[a]	ABE[b]
Vegetable oils							
Density	HHV = 46.502 - 11.259ρ (4)	36.9	0.451	1.479	0.148	0.592	0.005
Viscosity	HHV = 36.600 - 0.00274μ (5)	35.1	0.450	1.546	0.146	0.825	0.011
Flash point	HHV = 35.000 + 0.00610β (6)	54.8	0.382	1.739	0.057	0.815	0.008
Alkanes							

Density	HHV = 70.800 - 37.700ρ	(7)	98.7	0.582	2.895	0.007	0.696	0.010
Viscosity	HHV = 44.500 - 0.900μ	(8)	0.1	5.052	452.210	0.965	8.369	0.696
Alcohols								
Density	HHV = -100 + 171ρ	(9)	86.4	2.336	20.742	0.070	4.193	0.316
Viscosity	HHV = 7.660 + 9.95μ	(10)	80.1	2.831	185.130	0.105	5.912	0.607

[a]Average absolute error. [b]Average bias error

For Vegetable oils,
HHV = -29.5 + 77.8ρ -0.0124μ + 0.00549β (4)
AAE = 0.515, ABE = 0.0051, R^2 =79.6%, S=0.9568 kJ/kg, P = 0.147, PRESS = 12.6905 kJ/kg

For, Alkanes,
HHV = 66.0322 – 38.3421ρ + 2.9392μ (5)
AAE = 0.0328, ABE = 7.27 x 10^{-5}, R^2 = 100%, S = 0.0159 kJ/kg, P = 0.002, PRESS = 0.5528 kJ/kg

For Alcohols,
HHV = -70.105 + 121.464ρ + 3.299μ (6)
AAE = 4.3876, ABE = 0.3129, R^2 = 88%, S = 3.102 kJ/kg, P = 0.360, PRESS = 745.1590 kJ/kg

Neglecting flash point variable (β) for vegetable oils, the correlation reduces to
HHV = 41.876 – 5.951ρ – 0.0015μ (7)
AAE = 0.8389, ABE = 0.0108, R^2 = 39.9%, S = 0.4926 kJ/kg, P = 0.362, PRESS = 3.2208 kJ/kg
Where ρ = density, μ = viscosity, β = flash point

The expressions as provided in Table 2 are the correlation between HHV and individual predictor variables for the three categories of fuel. Equations 11 to 14 represent the correlations obtained when considering the combinations of predictor variables. Looking closely (Table 2), the statistical parameters (R^2, S, PRESS statistics, *p*-value, AAE, ABE) confirm the correlation coefficient of HHV versus density to be highly predictive. The correlation coefficients were 36.9%, 98.7%, 86.4% for vegetable oils, alkanes, and alcohols respectively. Considering HHV versus viscosity, the predictive ability of the governing correlations (Table 2) decreases with the correlation coefficients of 35.1%, 0.1%, and 80.1% for vegetable oils, alkanes, and alcohols respectively. Figures 2 to 4 show the 3-dimensional relationships between the HHV and the predictor variables of density and viscosity for the three categories of liquid fuel.

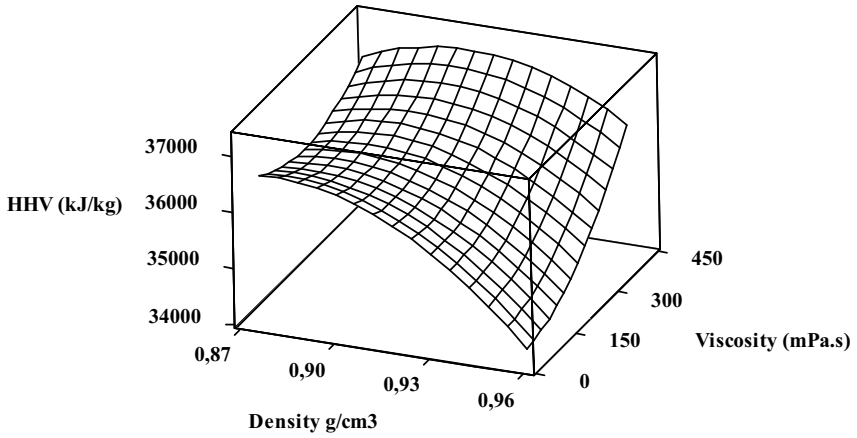


Figure 2: Relationships between higher heating value (HHV), density, and viscosity for vegetable oils

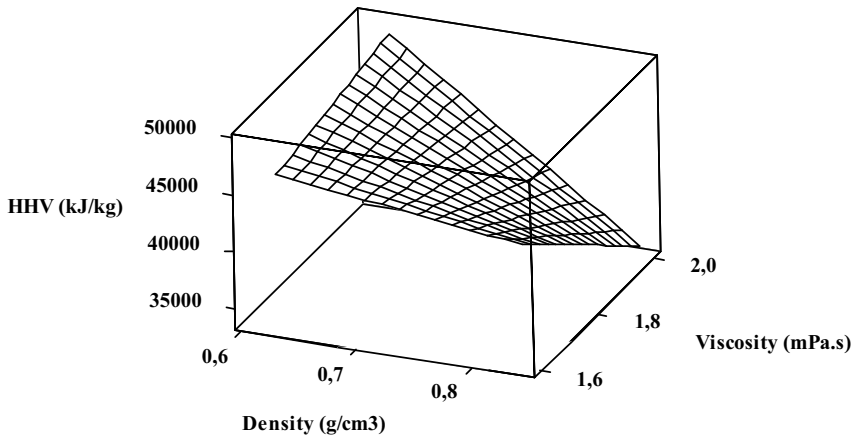


Figure 3: Relationships between higher heating value (HHV), density, and viscosity for alkanes

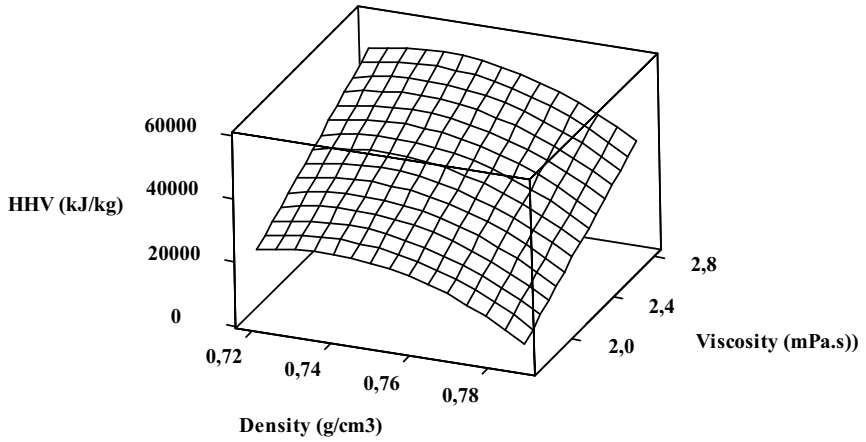


Figure 4: Relationships between higher heating value (HHV), density, and viscosity for alcohols

Other thing that may influence the HHV of liquid fuels is the chemical structure. Carbon atoms play a strong role in the resident energy of fuel materials. Relating to the chemical structure, if the number of carbon atom is increased, the longest chain will have a higher heat of combustion which releases more energy as a result of the breaking of bonds and the formation of new one. On the other hand, high hydrogen and oxygen contents lower the heating values of liquid fuels. From Table 2, the alkanes possess more HHV values than the other liquid fuels (vegetable oils and alcohols). For example, octane (C_8H_{18}) is 46,297 kJ/kg while linseed oil ($C_{57}H_{98}O_{12}$) is 39,960 kJ/kg and butanol ($C_{44}H_{10}O$) is 34,328 kJ/kg. This may be attributed to the more of the carbon atoms in the alkanes to less of hydrogen atoms in its molecule compared to vegetable oils and alcohols. The increase in the number of carbons and hydrogen as they relate to nitrogen and oxygen increases the higher heating value of a fuel [17]. Structurally, high oxygen content in fuels is related to low HHV [5].

3.2. Formulation and validation of the linear regression correlations

A faster, cheaper, reliable ways for predicting HHV is feasible [18]. This work tended to establish a robust way of estimating HHV from density, viscosity, and flash point data of three groups of liquid fuels. Validating these predictions is very crucial. Therefore, as enumerated in Section 2, the best representations of the correlations were chosen based on accurate statistical judgements. The HHV correlations development through the linear regression technique using the experimental data generated from the density, viscosity, and flash point (Table 1) of the fuels are as provided in Table 2 (Equations 4 to 10) and Equations (11) to (14). Among the eleven

correlations formulated, seven (Equations 4, 6, 7, 9, 11, 12 and 14) can be selected to be suitable for adequate predictions for the three liquid fuel groups. When considering vegetable oils, the relationship of HHV versus density (R^2 = 36.9%, S = 0.451 kJ/kg, *p*-value = 0.148, PRESS = 1.479 kJ/kg, AAE = 0.592, ABE = 0.005) or HHV versus flash point (R^2 = 54.8%, *p*-value = 0.005, S = 0.382 kJ/kg, PRESS = 1.739 kJ/kg, AAE = 0.815, ABE = 0.008) or HHV versus density, viscosity, and flash point (R^2 = 79.6%, *p*-value = 0.147, S = 0.957 kJ/kg, PRESS = 12.690 kJ/kg, AAE = 0.515, ABE = 0.005) or HHV versus density and viscosity (R^2 = 39.9%, *p*-value = 0.362, S = 0.493 kJ/kg, PRESS = 3.221 kJ/kg, AAE = 0.839, ABE = 0.011) should be appropriate. Though the relationship of HHV versus density for vegetable oils has a low regression coefficient of 36.9%, it can be noted that there is a symmetry of distribution of the residuals versus the fitted values plot (Figure 5) which makes some of the residual values close to the zero line, making this correlation highly predictive. Considering these four correlations representing the vegetable oils group, Equation 11 may be selected having the best predictive accuracy. This correlation includes in its model the three parameters of density, viscosity, and flash points. With the alkanes liquid fuels, the relationship of HHV versus density (R^2 = 98.7%, *p*-value = 0.007, S = 0.582 kJ/kg, PRESS = 2.895 kJ/kg, AAE = 0.696, ABE = 0.010) or HHV versus density and viscosity (R^2 = 100%, *p*-value = 0.002, S = 0.016 kJ/kg, PRESS = 0.553 kJ/kg, AAE = 0.033, ABE = 7.27×10^{-5}) should be appropriate. Based on the statistical assessments of these two correlations, Equation 12 represents better predictive accuracy with the inclusion of two predictors, density and viscosity, in the model. Also, considering the alcohols liquid fuel group, the relationship of HHV versus density (R^2 = 86.4%, *p*-value = 0.070, S = 2.3360 kJ/kg, PRESS = 20.742 kJ/kg, AAE = 4.193, ABE = 0.316) will be appropriate. For the highly correlated regression model fit, a further identification of the set of data was also evaluated based on the precise symmetry of the residuals versus the fitted values as shown in Figure 5. This was necessary in order to arrive at the simplest, the best, and the most accurate correlation to predict HHV. In addition, experimental HHV to the predicted HHV were compared for the groups of liquid fuels. Looking closely (Figure 6), data show acceptable limits with most of the values closer to the diagonal line indicating a perfect fit between the experimental and predicted HHV values.

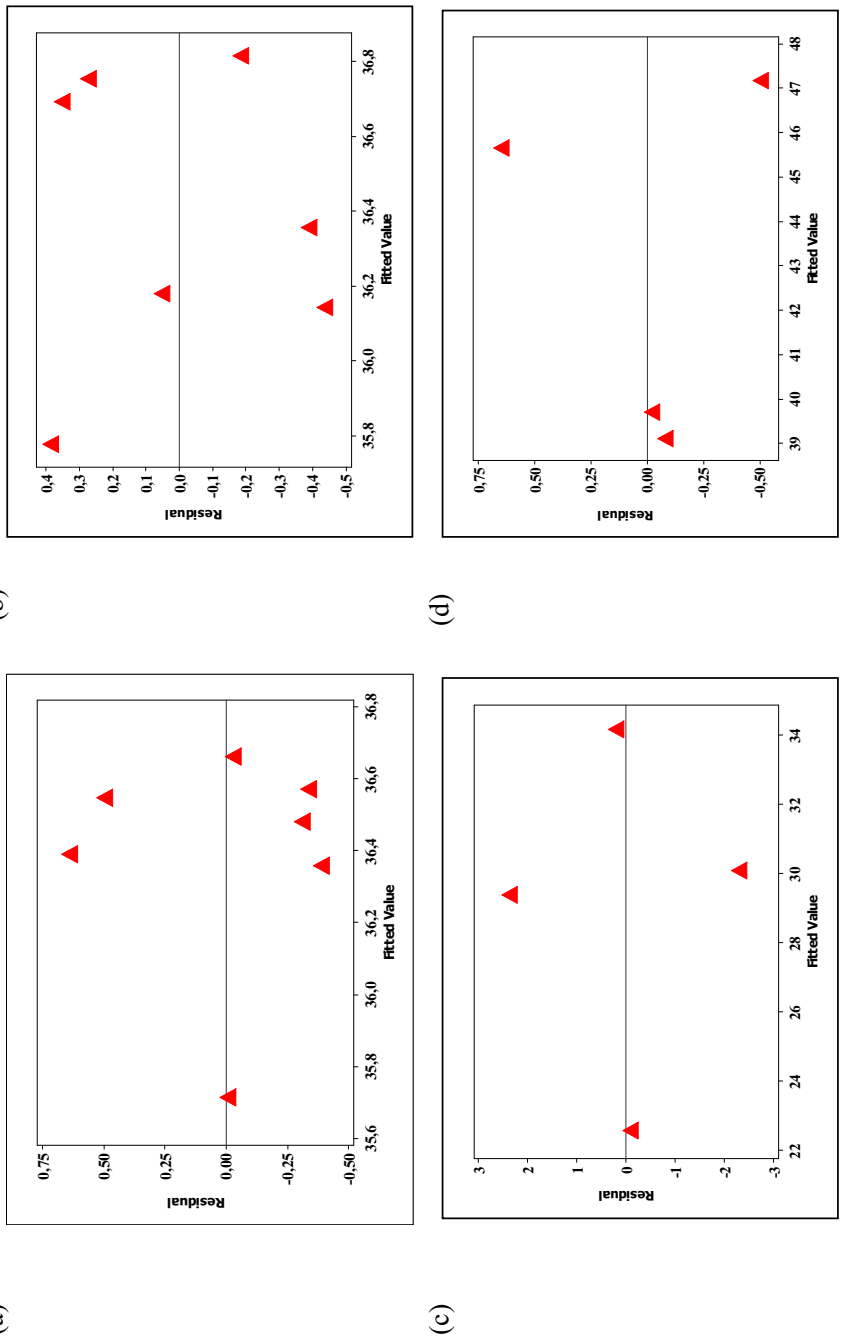
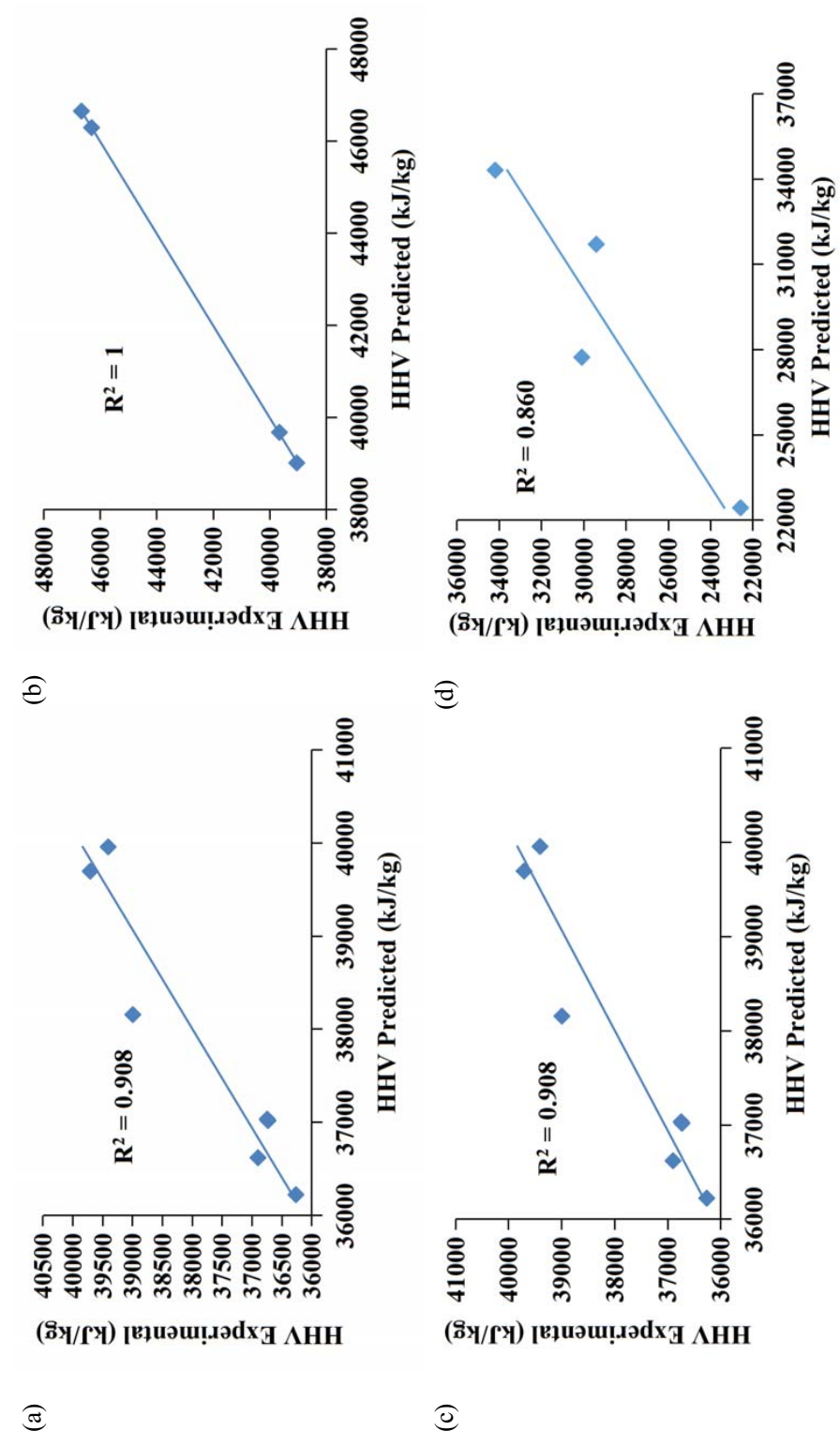


Figure 5. Diagnosis for the regression model fit of the correlated model for (a) vegetable oils (HHV and density values); (b) vegetable oils (HHV and flash point values) (c) alcohols (HHV and density values) (d) alkanes (HHV and density values)


(a)
HHV Experimental (kJ/kg)
HHV Predicted (kJ/kg)
R² = 0.908
40500
40000
39500
39000
38500
38000
37500
37000
36500
36000
36000 37000 38000 39000 40000 41000
(b)
HHV Experimental (kJ/kg)
HHV Predicted (kJ/kg)
R² = 1
48000
46000
44000
42000
40000
38000
38000 40000 42000 44000 46000 48000
(c)
HHV Experimental (kJ/kg)
HHV Predicted (kJ/kg)
R² = 0.908
41000
40000
39000
38000
37000
36000
36000 37000 38000 39000 40000 41000
(d)
HHV Experimental (kJ/kg)
HHV Predicted (kJ/kg)
R² = 0.860
36000
34000
32000
30000
28000
26000
24000
22000
22000 25000 28000 31000 34000 37000

7

Figure 6. Comparison between HHV experimental and predicted values from models for (a) vegetable oils correlation with density, viscosity, and flashpoints (b) alkanes correlation with density and viscosity (c) alcohols correlation with density and viscosity, and, (d) alcohols correlation with density

4. Conclusions

This study has brought to fore that instead of relying on expensive experimental instrumentation to estimate higher heating values of some liquid fuels, very robust and accurate relationships can be applied with the aid of simple physical tests like density, viscosity, flash points measurements. These simple tests are characteristics of liquid fuels. Mathematical correlations were developed to estimate the higher heating values of vegetable oils, alkanes, and alcohols from measured parameters of density, viscosity, and flash points. The developed correlations were statistically validated using reliable tools such as standard error of estimate, S, coefficient of determination, R^2, predicted residual error of the sum of square statistics, PRESS, error estimations (average bias error, ABE, and AAE, average absolute error), and the residual versus fitted values plot. The developed predictive correlations showed perfect agreement with the experimental values. It can be concluded that the alkanes have the highest heating value amongst other liquid fuels investigated in this study. Hexane had the highest high heating value of 46,655 kJ/kg. When considering vegetable oils, HHV versus density, viscosity, and flash point correlation is accurate (R^2 = 79.6%, *p*-value = 0.147, S = 0.957 kJ/kg, PRESS = 12.690 kJ/kg, AAE = 0.515, ABE = 0.005). For alkanes, HHV versus density and viscosity is accurate (R^2 = 100%, *p*-value = 0.002, S = 0.016 kJ/kg, PRESS = 0.553 kJ/kg, AAE = 0.033, ABE = 7.27 x 10^{-5}). For alcohols, HHV versus density is accurate (R^2 = 86.4%, *p*-value = 0.070, S = 2.3360 kJ/kg, PRESS = 20.742 kJ/kg, AAE = 4.193, ABE = 0.316).

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