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Prediction of higher heating values of biomass from proximate and ultimate analyses

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Abstract

Two new empirical correlations based on proximate and ultimate analyses of biomass used for prediction of higher heating value (HHV) are presented in this paper. The correlations have been developed via stepwise linear regression method by using data of biomass samples (from the open literature) of varied origin and obtained from different geographical locations. The correlations have been validated via incorporation of additional biomass data. The correlation based on ultimate analysis (HHV = 0.2949C + 0.8250H) has a mean absolute error (MAE) lower than 5 % and marginal mean bias error (MBE) at just 0.57 % which indicate that it has good HHV predictive capability. The other correlation which is based on proximate analysis (HHV = 0.1905VM + 0.2521FC) is a useful companion correlation with low absolute MBE (0.67 %). The HHV prediction accuracies of 12 other correlations introduced by other researchers are also compared in this study.

Keywords: Higher heating value (HHV); proximate analysis; ultimate analysis

1. Introduction

One of the most pressing global issues in recent times is the worldwide energy crisis which is predominantly attributed to earth's fast depleting fossil fuel resource. To address this predicament, many countries have heavily promoted the use of alternative fuel sources such as agricultural wastes as biomass fuel to generate heat and electricity. The benefit of utilizing such fuel for small-scale combustion or thermochemical conversion is apparent since they are renewable resources that can provide inexpensive auxiliary fuel. At the same time, such application provides an opportunity to solve their disposal problem.

The design and operation of biomass combustion systems rely substantially on several biomass characteristics, namely, heating value, moisture, ash content and elemental composition [1-3]. The heating value of a fuel can be reported in terms of a 'lower' (LHV) or 'higher' (HHV) value. The heating value of a biomass fuel can be determined experimentally by employing an adiabatic bomb calorimeter which measures the enthalpy change between reactants and products [2]. The use of bomb calorimeter, though relatively simple and accurate, may not always be accessible to researchers. To circumvent this problem, researchers with possession of an elemental analyzer usually conduct proximate or ultimate analysis and subsequently use the resulting data to determine the heating value via established empirical correlations. Proximate analysis is used to determine the weight percentages (wt %) of moisture, volatile matter (VM), fixed carbon (FC) and ash of a biomass while ultimate analysis is used to determine the weight percentages of chemical elements (carbon, hydrogen, nitrogen, oxygen and sulfur) of a biomass.

There were many previous attempts made to correlate the HHV with data from proximate and ultimate analyses. One of the earliest and most popular correlations was the Dulong correlation [4] first introduced in the late 1800's and based on data from ultimate analysis of coal. Over the past two decades, emphasis on renewable fuels has led many researchers to find empirical correlations based on data from proximate and ultimate analyses of biomass fuels, with particular focus on agricultural wastes. Tillman [5] suggests that HHV of biomass material is a very strong function of its carbon content and a popular correlation used to estimate the HHV of wood and wood bark ($HHV = 0.4373C - 1.6701$) is subsequently created. There are also researchers that propose HHV correlations based on experimental characterization of combined organic-based compounds (i.e. biomass and non-biomass materials). For example, Ahmaruzzaman [6] introduces several empirical HHV correlations based on the proximate analyses data obtained from co-cracking of petroleum vacuum residue with coal, plastics and biomass.

In this study, two new empirical correlations based on proximate and ultimate analyses of biomass (lignocellulosic compounds) used for prediction of HHV are presented. The predictive accuracies of the correlations are compared with recent and established biomass-based HHV correlations. These two correlations afford an easier, more cost-effective and faster alternative to predict HHV and are particularly useful for researchers without access to the comparatively more expensive and sophisticated equipments for experimental HHV determination.

2. Methodology

A database of proximate and ultimate analyses data as well as experimental HHV of biomass samples were obtained from the open literature and presented in Table 1. In order to enable wide and universal applicability of the proposed correlations, the database included 44 sets of data from previous studies conducted by researchers from Argentina, Australia, Cuba, Greece, India, Morocco, the Netherlands, Spain, Turkey and the United States of America. In addition, the types of biomass listed in the database vary widely from agricultural by-products (e.g. rice husk and corn straw) to wood (e.g. willow and oak). Another criterion for data inclusion in Table 1 was that the previous studies must include both proximate and ultimate analyses results to ensure completeness of the present study. For all the 44 biomass samples, it was be observed that VM, C and HHV ranges were within 60 – 90 wt%, 35 – 55 wt% and 14 – 23 MJ/kg, respectively. Another nine biomass samples were randomly selected from open literature and added in Table 1 solely for the purpose of validation of developed HHV correlations.

Table 2 provides the summary of recent and established correlations used for predicting the HHV of biomass. Six of the correlations are derived from proximate analyses while the other six are derived from ultimate analyses. Equations 1-9 represent the relatively newer correlations while equations 10-12 are relatively established and widely used by present researchers.

New correlations were formulated by means of linear regression analyses. Data and equations from Tables 1 and 2 were inserted into *Microsoft Excel* spreadsheets and subsequently regression statistics as well as analysis of variance (ANOVA) results were generated based on the best available fit. Two statistical parameters were used to evaluate the newly developed correlations, namely, mean absolute error (MAE) and mean bias error (MBE):

$$\text{MAE} = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{HHV_{predicted} - HHV_{\exp erimental}}{HHV_{\exp erimental}}\right| \times 100\%$$

$$\text{MBE} = \frac{1}{n}\sum_{i=1}^{n}\left[\frac{HHV_{predicted} - HHV_{\exp erimental}}{HHV_{\exp erimental}}\right] \times 100\%$$

MAE basically quantifies (based on the average of the set data) how close the predicted HHVs are to the experimental values in which lower MAE indicates higher accuracy of a particular correlation. For MBE, a positive value indicates an overall over-estimation while a negative value indicates an overall under-estimation of the sample population. The smaller the absolute value of MBE, the smaller the bias of the correlation [2].

3. Results and Discussion

3.1 Linear regression analyses

The initial regression attempt encompasses all the proximate or ultimate analyses variables (VM, FC, ash for proximate and C, H, N, O, S for ultimate) and *y*-intercept is allowed. This yields equations with low R^2 and *adjusted* R^2 (< 0.8) which clearly indicate the need to redo the regression. It should be noted that R^2 basically measures the goodness-of-fit in the regression analysis while *adjusted* R^2 is a modification of R^2 that will not be inflated unnecessarily by addition of variables (i.e. only presence of important variables that contribute to the overall physical meaning of HHV will increase the *adjusted* R^2 value). By forcing the constant to zero value, it is discovered that both R^2 and *adjusted* R^2 increase to more than 0.97. Since R^2 values are favorable for zero constant values, such practice is repeated for subsequent regression attempts.

Another significant observation is that the *p*-values for the coefficients of ash, N, O and S variables are higher than 0.05, implying that these variables do not contribute to the overall physical interpretation of the HHV. The author therefore, proceeds with stepwise regression where variables are either added or deleted to increase the *adjusted* R^2 value. By not selecting the aforesaid variables, two separate equations (Eqs. 13 and 14) with favorable regression statistics have been formulated (Table 3). The presence of VM, FC, C and H variables in the two equations is apt since it is well-established that carbon and hydrogen (elemental constituents that form volatile organic matter and fixed carbon) contribute significantly to biomass energy content [2]. The two equations are rather simple compared to most of the recent correlations (Eqs. 2, 3, 5, 6, 7, 9).

3.2 Accuracy and comparison with recent and established correlations.

By using data from Table 1, HHVs have been predicted by using all the 14 equations. Fig. 1 shows the comparison between predicted and experimental HHV for the developed correlations (Eqs. 13 and 14). It can be seen that most of the plotted values remain close to the curve of $HHV_{predicted} = HHV_{experimental}$, indicating good accuracy of the correlations. Eq. 14 seems to be marginally more accurate compared to Eq. 13 judging by the presence of more outliers (points outside the $\pm 5\%$ relative error lines) produced by the latter.

Fig. 2 shows the MAE and MBE (with respect to experimental values of HHV) of the developed correlations (Eqs. 13 and 14) and their comparison with recent and established empirical correlations (Eqs. 1 – 12). The 14 correlations are capable of predicting biomass HHVs with MAE lower than 7 %, indicating their good universal applicability. Correlations developed from proximate analyses (Eqs. 3, 8, 9 and 10) exhibit the four highest MAE values while correlations developed from ultimate analyses have the six lowest MAE values among the 14 correlations. This strongly suggests that correlations developed from ultimate analyses can generally provide HHV predictions with higher accuracy. This observation is consistent with a study reported by Sheng and Azevedo [2] where they suggest that 'ultimate analysis quantifies the elemental contents providing more detailed chemical composition on biomass'. It is possible that the carbon group contribution variables (VM and FC) provide an oversimplification aspect to the actual energy content of biomass resulting in reduced predictive accuracy compared to ultimate analysis variables which are elemental in nature.

Eq. (14) has the lowest MAE at 4.01 % and provides marginal over-estimation at just 0.57 % which strongly reflect its good HHV predictive capability. Eqs. (4) and (5) developed by Sheng and Azevedo [2] also exhibit good accuracy in HHV predictions since they both have comparable MAE and MBE. The author surmises the inclusion of C and H and exclusion of non-energy contributing variables such as N, S and ash render Eq. (14) more relevant in the context of predicting gross calorific value of biomass. Eq. (13) is also useful for predicting HHV of biomass by using proximate analyses data and it is a valuable companion correlation to Eq. (14) since the former has the lowest absolute MBE (0.67 %) among all the correlations developed from proximate analyses data. Admittedly, application of both Eqs. (13) and (14) may be limited to only lignocellulosic materials, nonetheless, application of these correlations can be incorporated in the design of small-scale biomass combustors, thermochemical converters or even industrial waste-to-energy biomass plants. Future statistical studies should be conducted to shed light on such application.

4. Conclusions

Two new empirical correlations (Eqs. 13 and 14) based on proximate and ultimate analyses of biomass have been developed via linear regression method for prediction of HHV. These correlations are easy to apply via simple manual calculation and require only carbon and hydrogen contents or volatile matter and fixed carbon contents (both on wt% dry biomass basis). They have important implications for affording combustion scientists with additional prediction alternatives with regards to biomass heating values analysis.

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Table 1

Composition and HHV of several biomass types used in this study.

Type	Proximate analysis (wt%)[a]			Ultimate analysis (wt%)[a]					Experimental HHV (MJ/kg)	Reference
	VM	FC	Ash	C	H	N	O	S		
Pistachio soft shell	67.85	8.69	14.21	45.53	5.56	1.74	47.17	-	18.57	[7]
Coconut shell	77.19	22.10	0.71	50.22	5.70	43.37	-	-	20.50	[4]
Wheat straw	82.12	10.98	6.90	42.95	5.35	-	46.99	-	17.99	[4]
Rice husk	61.81	16.95	21.24	38.50	5.20	0.45	34.61	-	14.69	[4]
Sugarcane bagasse	83.66	13.15	3.20	45.48	5.96	45.21	0.15	-	18.73	[4]
Bamboo wood	86.80	11.24	1.95	48.76	6.32	0.20	42.77	-	20.55	[4]
Olive stones	78.30	19.50	2.20	49.00	6.10	0.80	42.00	-	20.23	[8]
Almond shell	80.50	18.40	1.10	48.80	5.90	0.50	43.70	-	19.92	[8]
Sunflower seed shell	84.70	11.70	3.60	51.70	6.20	1.00	41.10	-	17.60	[9]
Esparto plant	80.50	16.80	2.20	46.94	6.44	0.86	43.56	-	19.10	[10]
Shea meal	66.30	28.70	5.00	48.56	5.86	2.88	37.70	-	19.80	[11]
Sugarcane bagasse	81.50	13.30	5.20	43.79	5.96	1.69	43.36	-	17.70	[11]
Cotton stalk	76.10	18.80	5.10	47.07	4.58	1.15	42.10	-	17.40	[11]
Peanut shell	84.90	13.40	1.70	47.40	6.10	2.10	44.40	-	18.60	[12]
Hazelnut shell	68.90	30.00	1.10	50.90	5.90	0.40	42.80	-	19.90	[12]
Dried grains - solubles	82.50	12.84	3.89	50.24	6.89	4.79	33.42	0.77	21.75	[13]
Wet grains	83.18	13.58	2.58	52.53	6.60	5.35	32.28	0.66	21.95	[13]
Corn stover	66.58	26.65	6.73	45.48	5.52	0.69	41.52	0.04	17.93	[13]
Coffee husk	78.50	19.10	2.40	47.50	6.40	-	43.70	-	19.80	[14]
Sugar cane straw	76.20	14.60	9.20	43.50	6.10	-	41.10	-	17.19	[14]
Marabú	81.30	17.20	1.50	48.60	6.30	-	43.60	-	20.72	[14]
Soplillo	77.80	20.70	1.50	48.80	6.50	-	43.20	-	22.58	[14]
C. equisetifolia leaf	73.50	16.46	3.93	46.12	6.90	1.18	42.64	-	18.48	[15]
L. Camara leaf	70.46	11.83	7.26	45.01	6.68	2.02	43.79	-	18.50	[15]
Oil palm fruit bunch	78.20	16.46	4.53	45.90	5.80	1.20	40.10	-	16.96	[15]
Olive kernel	63.90	32.80	1.70	54.60	6.80	0.80	36.10	-	22.40	[16]
Olive kernel shell	60.50	36.10	3.30	53.20	6.70	0.50	36.30	-	21.40	[16]
Olive cake	62.10	34.60	2.80	53.70	6.70	0.60	36.20	-	21.60	[16]
Olive kernel	73.62	24.25	2.13	52.44	6.17	1.32	37.85	0.09	19.90	[17]
Forest residue	79.80	20.00	0.20	53.16	6.25	0.30	40.00	0.09	19.50	[17]
Cotton residue	72.80	20.59	6.61	47.03	5.96	1.79	38.42	0.19	16.90	[17]
Alfalfa stems	78.92	15.81	5.27	47.17	5.99	2.68	38.19	0.20	18.67	[1]
Rice straw	65.47	15.86	18.67	38.24	5.20	0.87	36.26	0.18	15.09	[1]
Switch grass	76.69	14.34	8.97	46.68	5.82	0.77	37.38	0.19	18.06	[1]
Willow wood	82.22	16.07	1.71	49.90	5.90	0.61	41.80	0.07	19.59	[1]
Hybrid poplar	84.81	12.49	2.70	50.18	6.06	0.60	40.43	0.02	19.02	[1]
Almond hulls	73.80	20.07	6.13	47.53	5.97	1.13	39.16	0.06	18.89	[1]
Oak wood (small branch)	77.45	18.50	4.05	48.76	6.35	2.81	42.08	-	19.20	[18]
Oak wood (medium branch)	80.82	16.18	3.00	48.62	6.52	2.58	42.28	-	19.24	[18]
Oak wood (large branch)	81.75	16.18	2.07	48.57	6.81	2.39	42.23	-	19.17	[18]
Pine chips	72.40	21.65	5.95	49.66	5.67	0.51	38.07	0.08	19.79	[19]
Corn straw	73.15	19.19	7.65	44.73	5.87	0.60	40.44	0.07	17.68	[19]
Rape straw	76.54	17.81	4.65	46.17	6.12	0.46	42.47	0.10	18.34	[19]
Palm kernels	77.28	17.59	5.14	48.34	6.20	2.62	37.44	0.26	20.71	[19]
B-wood[b]	76.53	21.62	1.85	50.26	6.91	1.03	39.66	-	20.05	[19]
Pepper plant[b]	64.71	20.86	14.44	36.11	4.26	2.72	41.86	0.49	15.39	[19]
Biomass mix[b]	69.36	18.14	12.49	49.59	5.79	2.43	28.87	0.74	18.40	[19]
Sugarcane bagasse[b]	82.60	14.70	2.70	47.20	7.00	-	43.10	-	17.32	[14]
Ipil ipil[b]	79.90	17.70	2.40	48.30	6.80	-	42.50	-	20.22	[14]
Rice husk[b]	61.20	16.30	22.50	38.20	5.60	-	33.70	-	16.47	[14]
Olive pitts[b]	82.00	16.28	1.72	52.80	6.69	0.45	38.25	0.05	21.59	[1]
Pistachio shell[b]	81.64	16.95	1.41	50.20	6.32	0.69	41.15	0.22	18.22	[1]
Almond shells[b]	76.00	20.71	3.29	49.30	5.97	0.76	40.63	0.04	19.49	[1]

[a]Proximate and ultimate analyses are in terms of wt% dry biomass basis.
[b]Additional biomass data for validation of the HHV correlations.
'-' denotes undetected element content.

Table 2

Summary of recent and established correlations used for predicting the HHV of biomass.

No.	Equation[a]	Based on	Unit	Reference
Eq. (1)	$HHV = 19.914 - 0.2324Ash$	Proximate analysis	MJ/kg	Sheng and Azevedo [2]
Eq. (2)	$HHV = -3.0368 + 0.2218VM + 0.2601FC$	Proximate analysis	MJ/kg	Sheng and Azevedo [2]
Eq. (3)	$HHV = 0.3536FC + 0.1559VM - 0.0078Ash$	Proximate analysis	MJ/kg	Parikh et al. [20]
Eq. (4)	$HHV = 0.3259C + 3.4597$	Ultimate analysis	MJ/kg	Sheng and Azevedo [2]
Eq. (5)	$HHV = -1.3675 + 0.3137C + 0.7009H + 0.0318O^{*b}$	Ultimate analysis	MJ/kg	Sheng and Azevedo [2]
Eq. (6)	$HHV = 3.55C^2 - 232C - 2230H + 51.2C*H + 131N + 20{,}600$	Ultimate analysis	kJ/kg	Friedl et al. [3]
Eq. (7)	$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211*Ash$	Ultimate analysis	MJ/kg	Channiwala and Parikh [4]
Eq. (8)	$HHV = 354.3FC + 170.8VM$	Proximate analysis	kJ/kg	Cordero et al. [8]
Eq. (9)	$HHV = 35{,}430 - 183.5VM - 354.3Ash$	Proximate analysis	kJ/kg	Cordero et al. [8]
Eq. (10)	$HHV = -10.8141 + 0.3133 (VM + FC)$	Proximate analysis	MJ/kg	Jimennez and Gonzales [21]
Eq. (11)	$HHV = -0.763 + 0.301C + 0.525H + 0.064O$	Ultimate analysis	MJ/kg	Jenkins and Ebeling [22]
Eq. (12)	$HHV = 0.4373C - 1.6701$	Ultimate analysis	MJ/kg	Tillman [5]

[a]Dry biomass basis (wt%).
[b]O* is the sum of the contents of oxygen and other elements in the organic matter (O*= 100-C-H-Ash).

Table 3

Developed HHV correlations and their regression statistics.

No.	Equation	Based on	Unit	R^2	Adjusted R^2	Standard error	Significance *F*	*p*-value
Eq. (13)	HHV = 0.1905VM + 0.2521FC	Proximate analysis	MJ/kg	0.9953	0.9714	1.3507	1.24×10^{-48}	Both variables < 0.05
Eq. (14)	HHV = 0.2949C + 0.8250H	Ultimate analysis	MJ/kg	0.9976	0.9737	0.9684	1.47×10^{-54}	Both variables < 0.05

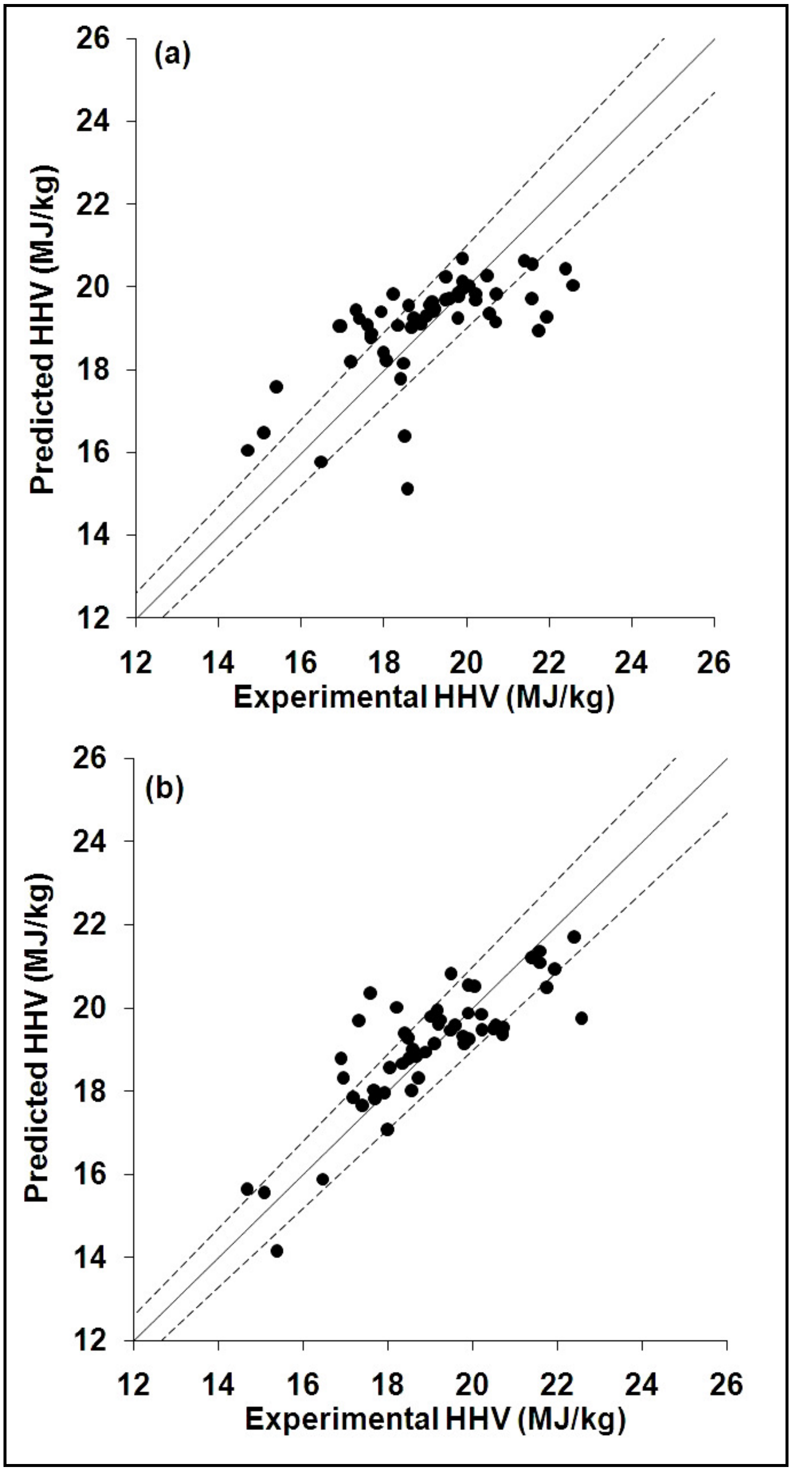

Fig. 1. Comparison between predicted and experimental HHV for the developed correlations based on (a) proximate analysis - Eq. (13); and (b) ultimate analysis - Eq. (14). Dashed lines indicate the ± 5% relative error.

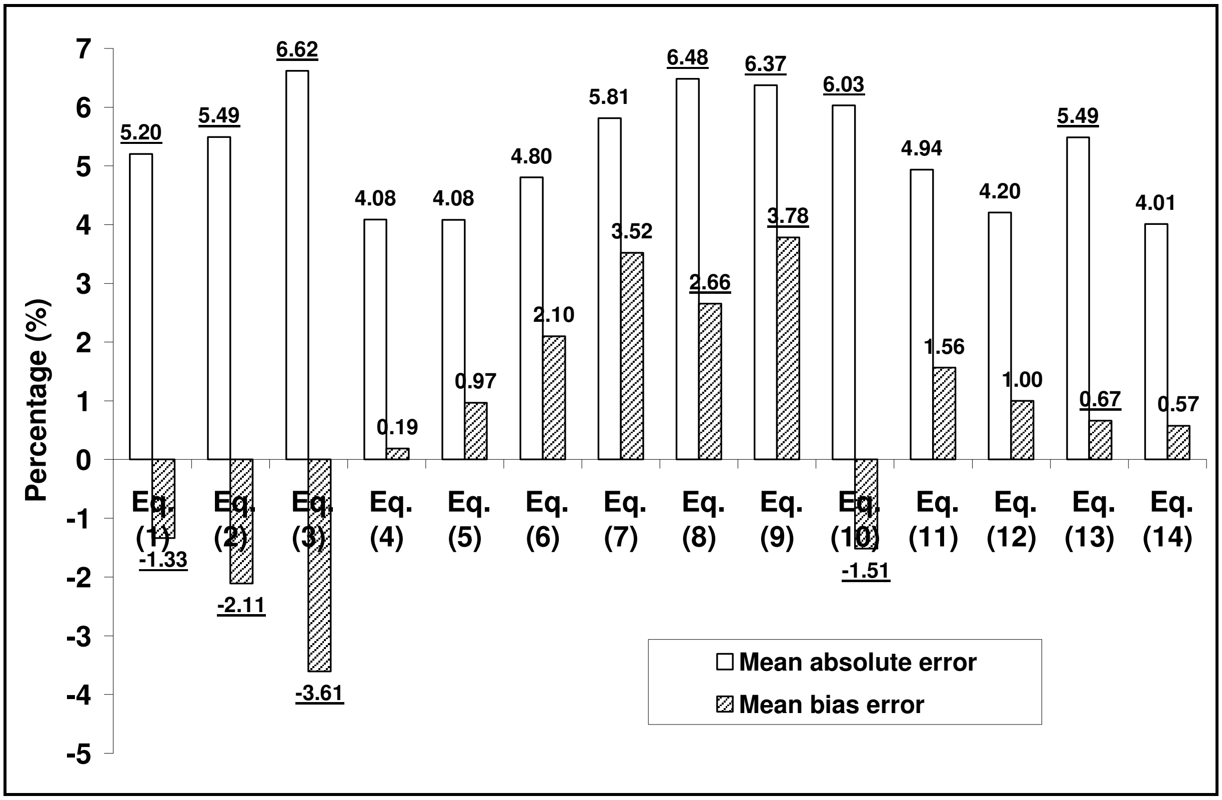

Fig. 2. MAE and MBE (with respect to experimental HHV) of the 14 correlations. Underlined values pertain to correlations developed from proximate analysis while non-underlined values pertain to correlations developed from ultimate analysis.