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## Prediction of Heating Values of Oil Palm Fronds from Ultimate Analysis

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**Abstract:** The heating value is one of the most important properties of biomass materials, as it can be used for design calculations or numerical simulations of the thermal conversion systems of biomass. The heating value can be determined experimentally or numerically. The determination of the heating value experimentally (by using a bomb calorimeter) involves laborious measurements while an ultimate analysis can be performed using automatic equipment. In this study, a multiple linear regression analysis was used to develop an empirical equation for the estimation of the higher heating value of Oil Palm Fronds (OPFs) using an ultimate analysis. An empirical equation based on the main elements carbon, hydrogen and oxygen ( $HHV = 0.879C + 0.321H + 0.056O - 24.826$ ) was the most accurate model, with a correlation coefficient ( $R^2$ ) of 0.92, Average Absolute Error (AAE) of 1.4% and Average Bias Error (ABE) of 0.16%.

**Key words:** Heating value, oil palm fronds, ultimate analysis, regression analysis

### INTRODUCTION

The steep rise in greenhouse emissions ( $CO_2$ ) generated by the combustion of fossil-fuels and the sustainable energy needs for the future motivate development of renewable energy sources and advance energy technologies. Nowadays, biomass is getting increased attention as one of the potential sources of renewable energy. Furthermore, biomass has the flexibility of using different thermochemical conversion processes such as combustion, pyrolysis and gasification technology (Li *et al.*, 2009; Gordillo and Annamalai, 2010). Knowing some of the biomass properties (heating value, moisture content, elemental composition, ash properties, etc) is essential for the design and operation of biomass thermochemical systems (Friedl *et al.*, 2005). Moreover, the proper design and operation of biomass conversion equipment rely significantly on the biomass properties.

The heating value (calorific value) of a biomass fuel defines its energy content which is one of the important parameters for designing conversion systems. Generally, the biomass heating value could be reported on two bases: (1) Higher Heating Value (HHV) and is in reference to the heat let off with the generated as well as original water in a

condensed state during the fuel combustion; (2) Lower Heat Value (LHV) which is related to the production of the gaseous water as the product (Sheng and Azevedo, 2005). The heating values of biomass materials can be determined experimentally by using an adiabatic bomb calorimeter or they can be calculated by using mathematical models based on the chemical composition, proximate or ultimate analysis of the biomass fuel (Sheng and Azevedo 2005; Yin, 2011). The experimental measurement of the biomass heating value is complicated, time consuming and involves manual laboratory work. On the other hand, ultimate, proximate and chemical analyses using typical or modern laboratory equipments are accomplished with ease, speed and less-expense (Sheng and Azevedo, 2005). Therefore, researchers who are concerned with biomass heating values would want to determine the heating value with an easy and fast method within an acceptable tolerance, based on the basic characteristics of the biomass (Akkaya, 2009).

Hence, there have been many attempts to estimate the heating value of biomass fuels based on chemical analysis (Demirbas, 2001; Sheng and Azevedo, 2005), proximate analysis (Parikh *et al.*, 2005) and ultimate analysis (Huang *et al.*, 2009). Moreover, Sheng and

Azevedo (2005) proposed correlations to estimate the heating values of biomass fuels, based on chemical, proximate and ultimate analyses and found that the correlations based on the ultimate analysis were the most accurate and reliable. However, the correlations based on the proximate analysis had low accuracy because the proximate analysis would provide only an empirical composition of the biomass while the correlations based on the chemical analysis were not reliable because of the variation of the component properties. Nevertheless, there has been no attempt contributed to oil palm fronds as a biomass fuel. Therefore, the objective of the present study is to develop correlations between the heating values and the ultimate analysis for oil palm fronds produced in Malaysia.

The OPF is one of the most abundant by-products produced in Malaysia during the harvesting and pruning time (Kawamoto *et al.*, 2001). The fronds consist of the petiole and leaflets and the structure of the fronds was found comparable to that of hardwood (Shuit *et al.*, 2009). Mohammed *et al.* (2005) found the chemical composition of the fronds to be as follow: 49.8% cellulose, 83.5% hemicellulose and 20.5% lignin. However, due to the high amount of cellulose and low amount of lignin, OPF considered as convenient feedstock for the gasification technology. Therefore, currently the OPF has started to be used as a feedstock for the gasification technology (Elneel *et al.*, 2011; Sulaiman *et al.* 2011).

**EXISTING MATHEMATICAL MODELS  
BASED ON THE ULTIMATE ANALYSIS**

There have been many proposed models for calculation of heating values based on chemical analysis, proximate analysis and ultimate analysis. The ultimate analysis based models reported by

Dulong’s (1880) was the first model developed for calculation of heating values which was intended for prediction of heating values for coal samples (Kathirvale *et al.*, 2003; Vargas-Moreno *et al.*, 2012).

Thereafter, many researchers proposed the variations of Dulong’s model, including new coefficients and sometimes new expressions (Vargas-Moreno *et al.*, 2012). In 1978, Tillman (cited in Yin, 2011; Vargas-Moreno *et al.*, 2012) developed two new equations (the second derived from the first) to estimate the heating value from the ultimate analysis for biomass fuels and suggested that the biomass heating value has a very strong function in its carbon content (HHV = 0.4373C-1.6701). However, Table 1 shows some of the more common models that have been used for coal and biomass. Demirbas *et al.* (1997) (cited in Vargas-Moreno *et al.*, 2012) proposed two empirical equations to predict the heating values for the hydrolytic oils of poplar trees and lignocellulose materials. The first one took into account the elements C, H and O while the second equation took into account the same elements plus N. A large quantity of biomass samples together with their higher heating values and the basic analysis data were collected from the open literature and used by Sheng and Azevedo (2005) to develop a series of models, two of these models were based on the results of ultimate analysis. Recently, proposal for a new model for a wide range of biomass materials are published in the literature (Friedl *et al.*, 2005; Thipkhunthod *et al.*, 2005; Huang *et al.*, 2009; Callejon-Ferre *et al.*, 2011; Yin 2011).

Generally, it can be noted that, carbon elements were taken into account for all the published models that were based on the ultimate analysis, due to the fact that carbon has a direct impact on the heating value. Moreover, some of these models also took into account the element hydrogen and oxygen. Nitrogen and sulfur were accounted in a few models.

Table 1: Models based on the ultimate analysis for coal and biomass

Researcher	Model	Biomass type	Remarks
Dulong (cited in Kathirvale <i>et al.</i> , 2003)	HHV = 8080C+34460H-43080+2250S	Coal	Original
Dulong (cited in Kathirvale <i>et al.</i> , 2003)	HHV = 81C+342.5 $\left( H - \frac{O}{8} \right) + 22.5S - 6(9H - W)$	MSW/Coal	Modified
Dulong (cited in Kathirvale <i>et al.</i> , 2003)	HHV = 144.5C+609.6H-76.2O+40S+10N	Coal	Modified
Dulong (cited in Kathirvale <i>et al.</i> , 2003)	HHV = 78.31C+359.32 $\left( H - \frac{O}{8} \right) + 22.12S + 11.8 + 5.78N$	Coal	Modified
Tillman (cited Yin, 2011)	HHV = 0.4373C-1.6701	Wood/bark	-
Demirbas <i>et al.</i> (1997)	HHV = (33.5C+142.3H-15.4O)×10 <sup>-2</sup>	Hydrolytic oils from poplar wood	-
	HHV = (33.5C+142.3H-15.4O-14.5N)×10 <sup>-2</sup>	Many kind of biomass	-
Demirbas (2001)	HHV = 0.3699C+1.3178	Wood, bark etc.	-
	HHV = 0.3856(C+H)-1.6938	Wood, bark etc.	-
Sheng and Azevedo (2005)	HHV = 0.3259C+3.456	Biomass	-
	HHV = -1.3675+0.3137C+0.7009H+0.0318O*	Biomass	-
Yin (2011)	HHV = 0.2949C+0.82510H	Biomass	-

W: wt% of water, O\*: Sum of the contents of the oxygen and other elements (including S, N, Cl, etc.) in the organic matter

**MATERIALS AND METHODS**

**Sample preparation:** The biomass material (OPF) used for these experiments was obtained from different places in the state of Perak in Malaysia. The sample collection was carried out throughout a six month period from August 2011 to January 2012. The biomass samples were first dried naturally and then dried further in a dryer oven at 105°C for 24 h. After drying, the samples were ground and sieved to fine size of 0.212 and 0.6 mm.

**Sample characterization:** The characterizations of the samples included the elemental analysis and determination of the higher heating value. The elemental analysis to find the percentages of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) content in the samples was carried out using LECO CHNS-932

elemental analyzer while the higher heating value was measured using the IKA Werke C5000 bomb calorimeter.

**Heating value model:** Biomass materials composed of the elements C, H, O, N and S, where the first three elements represented about 97-99% of the biomass organic mass. The relationships between the higher heating values and ultimate analysis components (C, H, O and N) are plotted in Fig. 1. Sulfur was found in a very small amount (less than 0.17%) and therefore it was not considered in the model. It can be observed from the same Fig. 1 that there is a linear relationship between the heating value with carbon, hydrogen and oxygen. However, the heating value increased with an increase in carbon and hydrogen content which agrees with the results of Sheng and Azevedo (2005). The heating values decreased with an

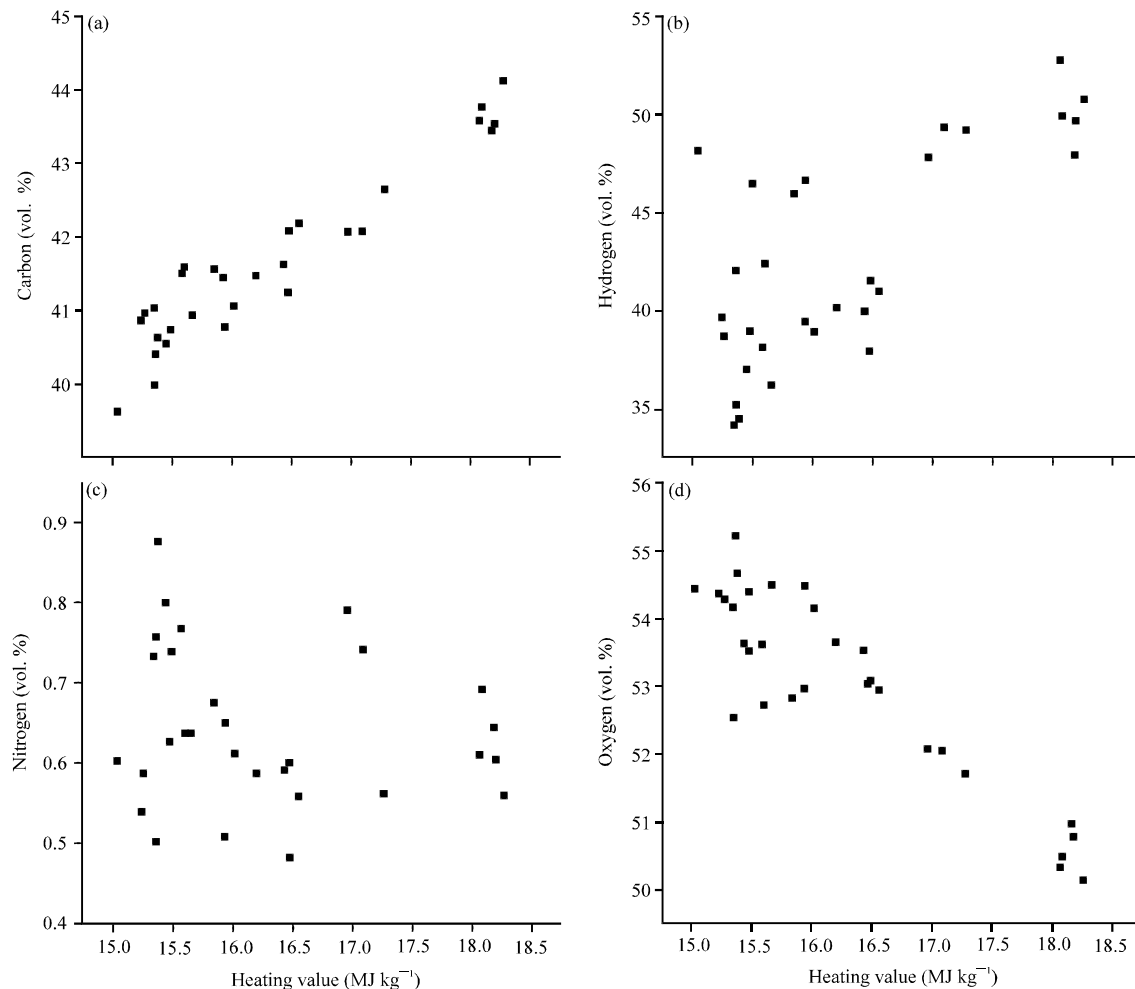


Fig. 1: Correlation between heating value of OPF and its ultimate analysis content

**Table 2:** Calculated and critical correlation coefficient for the biomass components

Components	Calculated correlation coefficient (R <sup>2</sup> )	Critical correlation coefficient (rt)
Carbon	0.903	0.361
Hydrogen	0.523	0.361
Oxygen	0.817	0.361
Nitrogen	0.026	0.361

increase in oxygen content and this correlates well with the fact that oxygen is not a reactive element (Sheng and Azevedo 2005). On the other hand, there is no trend observed between heating values and nitrogen content. Therefore, in calculating the higher heating value of the OPF, only three elements are selected which are carbon, hydrogen and oxygen. For the current experimental data and confidence level of 0.95%, there are significant correlations between the biomass heating value and the carbon, oxygen and hydrogen components; for which the correlation coefficients (R<sup>2</sup>) are 0.903, 0.817 and 0.523, respectively. On the other hand, there is no correlation between the nitrogen components (0.026) as shown in Table 2. From the same Table 2, it can be noted that the computed correlation coefficients for carbon, oxygen and hydrogen are greater than the critical correlation coefficients for the number of samples (Wheeler and Ganji, 2003).

The multiple linear regression analysis was adopted to develop an empirical equation to estimate the heating value of the OPF samples from the C, H and O percentages. The evaluations of the variables were also conducted at a significant confidence level of 0.95%. The procedure to create the equation and statistics analysis was developed by using spreadsheet software. The resulted empirical equation was next used to calculate the heating values which were then compared with those obtained experimentally.

## RESULTS AND DISCUSSION

**Development of models:** In the development of multiple linear regression models, carbon (C), hydrogen (H) and oxygen (O) were taken as input independent variables while the actual heating values are taken as an output dependent variable. In this study, four empirical equations were proposed to determine the heating values using the elements of the ultimate analysis. These equations were developed based on the fact that, the heating value of biomass is a function of carbon, carbon and hydrogen, carbon and oxygen and also as a function of carbon, hydrogen and oxygen. However, carbon was included in the entire proposed models; this is because of its

**Table 3:** Models based on the ultimate analysis elements

Independent		AAE ABE			
No. variables	Proposed model	R <sup>2</sup>	(%)	(%)	
M1	C	HHV = 0.924C-22.403	0.903	1.6	-0.0016
M2	C, H	HHV = 0.824C+0.2894H-19.427	0.916	1.5	0.16
M3	C, O	HHV = 0.886C+0.0324O+19.086	0.903	1.6	0.19
M4	C, H, O	HHV = 0.879C+0.3214H+0.056O-24.826	0.917	1.4	0.16

AAE: Average absolute error, ABE: Average bias error

nature as the major reactive element present in the biomass. The proposed models are shown in Table 3.

**Selection of the best model:** In selecting the best model, all equations were evaluated and compared with the fitting performance criteria which evaluated the accuracy and validity of the model. In this study, the considered performance criteria were the correlation coefficient (R<sup>2</sup>), Average Absolute Error (AAE) and Average Bias Error (ABE) which can be calculated as:

$$R^2 = 1 - \frac{\sum_{i=1}^n \frac{(\overline{HHV}_M - HHV_c)^2}{(\overline{HHV}_M - HHV_M)^2}}{n} \quad (1)$$

$$AAE = \frac{1}{n} \sum_{i=1}^n \left| \frac{HHV_c - HHV_M}{HHV_M} \right| \times 100\% \quad (2)$$

$$ABE = \frac{1}{n} \sum_{i=1}^n \frac{HHV_c - HHV_M}{HHV_M} \times 100\% \quad (3)$$

where, subscribes M and C denote the measured and calculated values for the higher heating value, respectively while  $\overline{HHV}_M$  is the measured average higher heating value of all the samples and n, is the number of samples. The correlation coefficient (R<sup>2</sup>) is used widely in statistical and regression analyses to quantify the accuracy of the model. The higher value of the correlation coefficient, indicates the better estimation (A perfect model has an R<sup>2</sup> of 1.0). The Average Absolute Error (AAE) of the correlation indicates the correlation accuracy. The lower the AAE value, the higher would be the accuracy of the correlation model. ABE describes the average bias error of the correlation. A positive value of ABE means an overall over-estimation while a negative value indicates an overall under-estimation of the sample population. The smaller is the absolute value of ABE is, the smaller would be the bias of the correlation. Table 3 shows the values of the R<sup>2</sup>, AAE and ABE for the proposed model equations. It can be seen that the model M4 gives the maximum R<sup>2</sup> and minimum AAE performance, according to that, the best model of predicting the heating value of the OPF by using the ultimate analysis could be:

$$HHV = 0.879C+0.3214H+0.056O-24.826 \quad (4)$$

Table 4: Comparison between measured and predicted heating values of the OPFs

Sample	Ultimate analysis (wt %)					Measured heating value (MJ kg <sup>-1</sup> )	Predicted heating value (MJ kg <sup>-1</sup> )	AAE (%)
	C	H	N	S	O			
1	42.290	3.924	0.770	0.060	52.956	16.014	16.572	3.485
2	40.800	3.937	0.498	0.015	54.774	15.774	15.367	-2.580
3	42.360	4.069	0.538	0.024	53.009	16.385	16.683	1.819
4	40.290	4.780	0.722	0.047	54.161	15.833	15.156	5.236
5	42.080	4.143	0.603	0.0036	53.138	15.981	16.468	3.047
6	40.970	5.000	0.744	0.078	53.208	15.409	15.771	2.351
OPF (Abdullah <i>et al.</i> , 2010)	42.100	5.460	0.700	0.130	47.460	15.590	16.590	6.416

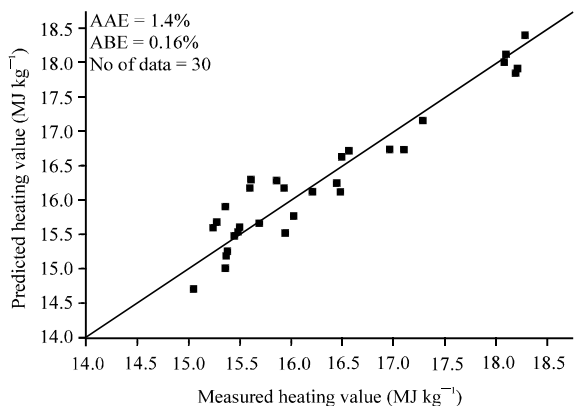


Fig. 2: Comparison between measured and calculated heating values of the oil palm fronds

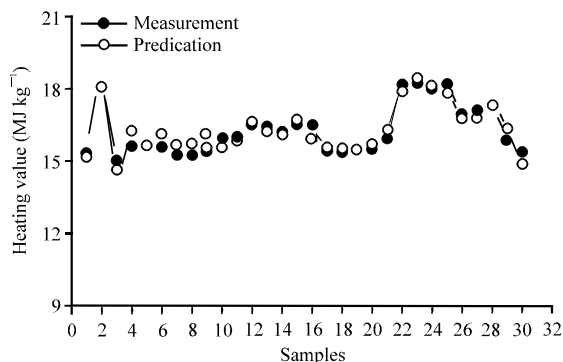


Fig. 3: Comparison of measured and predicted heating value

**Model validation:** Validation of the model was carried out by comparing the predicted heating values with those obtained experimentally. The predicted and measured values are shown in Fig. 2 and 3. It can be seen from the same Fig. 2 and 3 that the predicted values were quite consistent with the experimental measurements. Figure 4 shows the scatter plot of the standard residuals against the predicted heating values. It can be seen that the standard residuals were randomly distributed along the predicted heating values and most of the values lay within  $\pm 2$ .

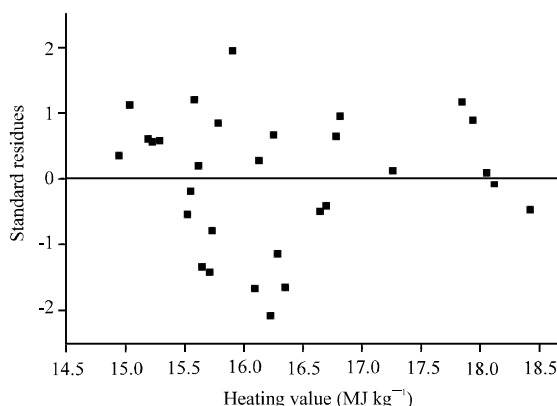


Fig. 4: Standard residuals against the predicted heating values

The developed model was also tested with six other samples of oil palm fronds (not included in developing the model) to confirm the reliability of the model. Table 4 shows the comparison between the measured and predicted heating values for the tested samples. However, the developed model is capable of predicting the heating value of oil palm fronds with an average absolute error of less than 6%, indicating its good predicting capability. In addition, the model was used to predict the heating value for the OPF sample reported in the literature (Abdullah *et al.*, 2010). The measured and predicted heating values are presented in Table 4, with an average absolute error of 6.42%, indicating its good applicability for Malaysian oil palm fronds.

### CONCLUSION

The multiple linear regression analysis was used to develop an empirical correlation for the prediction of the heating value of oil palm fronds based on the ultimate analysis. The predicted heating values calculated by the proposed correlation showed good agreement with experimental values. However, the results showed a correlation coefficient ( $R^2$ ) of 0.92, with an Average Absolute Error (AAE) and Average Bias Error (ABE) of 1.4 and 0.16%, respectively. Moreover, the results showed

that the predicted heating values were in agreement with those obtained by the experimental measurements. Therefore, the developed model may be acceptable for estimating the heating values of Malaysian oil palm fronds.

Correlations based on the proximate analysis and chemical analysis should be investigated in the future.

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