

ESTIMATING CALORIFIC VALUES OF LIGNOCELLULOSIC BIOMASS FROM VOLATILE AND FIXED SOLIDS

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Abstract

The gross calorific value (GCV) is the most important property of any fuel, which shows its energy content. The experimental determination of GCV of solid fuels is a cost intensive process, as it requires exceptional equipment and high skills. To streamline the task, many equations were developed in past for determining GCV from proximate and ultimate analysis of solid fuels. In present study two empirical equations were developed to predict the GCV of lignocellulosic biomass using their volatile solids (VS) and fixed solids (FS) with and without ash contents in specified range of VS (60.84–82.64 %), FS (17.36–39.16 %) and ash (1.59–21.76 %) as percentage dry mass basis. The experimental data was analyzed through multiple regression analysis and least square method. The empirical equations were developed and their mean errors were determined. The developed empirical equations are simpler, economical, less time consuming and are more accurate compare to the equations based on the proximate analysis.

Keywords: Calorific Value (CV), Lignocellulosic Biomass, Volatile Solids (VS), Fixed Solids (FS)

1. Introduction

Environmental and economic concerns of reducing greenhouse gas CO₂ emissions and of increasing fuel flexibility is motivated using biomass and its derived fuels to substitute fossil fuels for heat and electricity generation. Among the various conversion technologies, combustion is the most common and developed way of converting biomass to energy [1-2]. Biomass is an organic matter, which is available on a renewable basis and includes all plants (trees, agricultural crops, wood and wood residues, grasses, and aquatic plants) and plant derived materials (animal manure and municipal residues). It stores sunlight energy in chemical bonds. When the bonds between adjacent carbon, hydrogen and oxygen molecules are broken by digestion, combustion, or decomposition, these substances release their stored, chemical energy [3]. Agricultural wastes represent a prospective resource of energy not only in many developing countries, but also in developed ones. On average, the world's 15 % of primary energy consumption is supplied from biomass and this figure amounts more than 35 % when we refer only to developing countries [4-5]. Thermochemical processes represent the most developed options for exploitation of biomass, and among them direct combustion is the most common and developed way to convert it into the energy [1-2, 6].

The design and operation of biomass combustion systems significantly depend upon biomass characteristics such as the calorific value, moisture content, elemental composition, ash properties, etc. [7-8]. The calorific value (CV) is the most important

among them. It is usually measured in terms of energy content per unit mass (MJ/kg). The CV of biomass can be expressed in two forms, the gross calorific value (GCV) and the net calorific value (NCV). The GCV is the enthalpy of complete combustion of biomass that also includes the condensation enthalpy of the water formed during reaction. According to the technical specification CEN/TS 14918:2005 [9], GCV is defined as: "the absolute value of the specific energy of combustion, in joules, for unit mass of a solid biofuel burned in oxygen in a calorimetric bomb under the conditions specified. The products of combustion are assumed to consist of gaseous oxygen, nitrogen, carbon dioxide and sulfur dioxide, of liquid water (in equilibrium with its vapor) saturated with carbon dioxide under the conditions of the bomb reaction, and of solid ash, all at the reference temperature". However, the NCV is the enthalpy of complete combustion of biomass, with any water form formed remaining as vapor.

The GCV of biomass can be determined either experimentally or by using empirical equations. Experimental determination of GCV is done by utilizing an adiabatic bomb calorimeter, which measures the enthalpy change between reactants and products. The second method for determining GCV is by using empirical equations based on the ultimate or proximate analysis. Ultimate analysis is used to determine the mass percentages of chemical elements (carbon, hydrogen, nitrogen, oxygen and sulfur), whereas the proximate analysis is used to determine the mass percentages of moisture,

volatile matter (VM), fixed carbon (FC) and ash. The experimental determination of GCV and ultimate analyses requires special and expensive instrumentation, whereas proximate analyses data can be obtained with relative ease using common laboratory equipment (muffle furnace) [7]. In proximate analysis the moisture of biomass sample is determined when it is heated at 105 °C, until further loss of the mass will not occur, and VM is determined by heating sample at 950 °C in inert atmosphere, whereas the ash is usually determined by oxidizing at 815 °C and FC is generally obtained from 100 – (ash + VM). The procedure of biomass proximate analysis is shown in Fig. 1. Due to fusing of ash at 815 °C, some biomass samples may be analyzed for volatile matter contents only up to 750 °C [10].

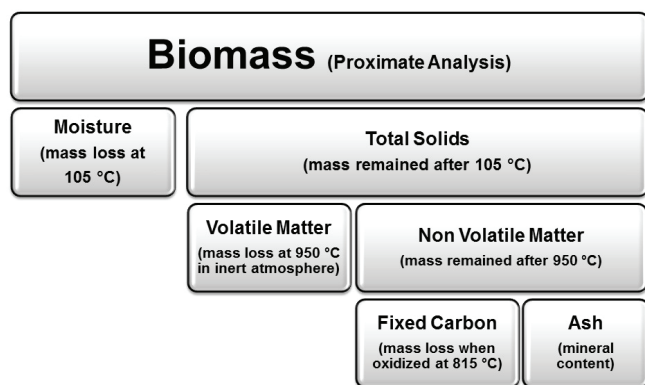


Figure 1. Procedure of proximate analysis of biomass

There are many equations exists in literature estimating the GCV of different fuels, out of those eight equations are given in Table 1 for estimating the GCV from proximate analysis of biomass based on percentage of dry mass basis. The objective of this study is to develop two new empirical equations for predicting the GCV of lignocellulosic biomass from their volatile solids (VS), fixed solids (FS) and without and with ash contents respectively. Lignocellulosic biomass refers to plant biomass that is composed of cellulose, hemicellulose, and lignin. It includes dedicated energy crops, agricultural residues, wood residues and municipal paper waste. The VS is the material that can be volatized and burned off when ignited at 550 °C and is presumed to be organic matter of the substance, whereas the concept of the fixed solids (FS) is used to represent the residue remained after total solids (TS) are ignited and oxidized at 550 °C [11]. The procedure for determination of biomass volatile and fixed solid is shown in Fig. 2. It is noted that the VS content is often used as the measure of the biodegradability of the organic fraction of biomass [12].

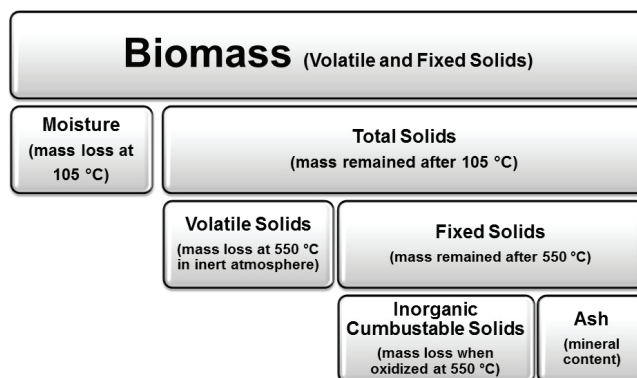


Figure 2. Procedure for determination of biomass volatile solids, fixed solid and ash

Table 1. Equations available in literature for GCV estimation from proximate analysis (% dry mass basis)

Eq. No.	Empirical Equation [GCV in MJ/kg]	MAE [%]	MBE [%]	Ref.
1	$GCV = 0.196 (FC) + 14.119$	8.88	-5.60	[13]
2	$GCV = 0.312 (FC) + 0.1534 (VM)$	7.69	-6.97	[13]
3	$GCV = 0.3543 (FC) + 0.1708 (VM)$	5.68	4.23	[14]
4	$GCV = 0.1905 (VM) + 0.2521 (FC)$	5.49	0.67	[15]
5	$GCV = 0.3133 (VM + FC) - 10.81408$	4.43	1.16	[16]
6	$GCV = 19.914 - 0.232 (ash)$	3.78	0.30	[17]
7	$GCV = 0.3536 (FC) + 0.1559 (VM) - 0.0078 (ash)$	3.74	0.12	[10]
8	$GCV = 0.2218 (VM) + 0.2601 (FC) - 3.0368$	3.65	0.26	[17]

2. Methodology

2.1. Analysis of biomass

The biomass material was collected with due care to get the most representative samples. After collecting the required samples, these were spread out on a plastic tray and were allowed to air-dry prior to milling. In general the material is considered as air-dried when the moisture content is less than 10 % by mass. The milled biomass samples were sieved and representative samples were then taken by conventional coning and quartering method for analysis.

Total solids (TS) content was determined by using ASTM E1756-08 standard method [18]. A sample of 2 g was taken into the pre-weighted silica crucible, which was dried at the temperature of 105 °C for one hour. The silica crucible containing sample was then placed into the oven at the temperature of 105 °C for six hours. Afterwards, the crucible was placed into the desiccator till its temperature reduces to room temperature and then crucible was weighed. Finally, the percentage of TS was determined by using Eq. 9 as the quantity of sample remained in the crucible.

$$TS = \frac{m_3 - m_1}{m_2 - m_1} \times 100 \quad (9)$$

Where, m_1 was the mass of crucible, m_2 was the mass of crucible and sample and m_3 was the mass of crucible plus residue after 105 °C. Percentage VS content was determined by ignition of dried samples in inert atmosphere at 550 °C [12]. After the TS determination as given above, the silica crucible was then placed into a muffle furnace at the temperature of 550 °C for 2 hours. The loss of mass on heating was the measure of VS and was determined by using Eq. 10. During this heating, a constant flow of nitrogen gas was purged through the muffle furnace in order to maintain the inert atmosphere.

$$VS = \frac{m_4 - m_1}{m_3 - m_1} \times 100 \quad (10)$$

Where, m_4 was the mass of crucible plus residue after heating at 550 °C. FS is the residue left after igniting the sample at 550 °C. It was calculated by subtracting VS from TS. The ash content was determined by using ASTM E1755-01(2007) standard method [19] and was the representation of the mass percent of residue remained after oxidation. During determination of ash, a constant flow of oxygen gas was purged through the muffle furnace in order to oxidize the biomass. GCV of biomass samples was experimentally measured by adiabatic bomb calorimeter according to the ASTM D5865-10ae1 standard method [20]. All analyses were done in duplicate and the results were expressed relative to the 105 °C oven-dried mass basis. The results of the VS, FS, ash and gross calorific value experimental (GCV_E) are given in Table 2.

Table 2. Results of biomass analysis

Sample No	Name of Biomass	(% by mass, dry basis)			GCV_E (MJ/kg)
		VS	FS	ash	
1	Bagasse	75.43	24.57	4.87	16.89
2	Banana Plant Trash	62.69	37.31	17.76	14.24
3	Barley straw	70.97	29.03	7.41	16.95
4	Canola Straw	68.64	31.36	10.49	16.22
5	Coconut coir	62.79	37.21	3.84	16.36
6	Corn Cob	71.98	28.02	7.05	16.63
7	Corn Stover	77.72	22.28	6.73	17.69
8	Cotton Gin Waste	60.84	39.16	21.76	14.33
9	Cotton Stalks	63.54	36.46	10.49	16.05
10	Groundnut shell	82.64	17.36	1.70	18.38
11	Mango Wood	80.78	19.22	3.89	18.08
12	Millet Stalks	69.28	30.72	9.27	16.65
13	Neem wood	79.98	20.02	1.59	20.02
14	Rice Husk	61.39	38.61	21.62	15.02
15	Rice Straw	62.27	37.73	19.39	14.50
16	Saw Dust	69.02	30.98	6.83	16.58
17	Soybean Straw	73.53	26.47	8.33	16.23
18	Sugarcane trash	66.42	33.58	13.95	15.60
19	Sunflower Stover	65.01	34.99	9.38	15.69
20	Sunflower seed shell	73.97	26.03	3.53	17.08
21	Wheat Straw	64.12	35.88	15.30	15.06
22	Wood Chips	78.69	21.31	5.93	19.92

2.2. Development of new equations

For the development of empirical equations, the data from Table 2 was taken into consideration and method of multiple linear regression analysis was used. This method helps to find out the relationship between two or more explanatory variables (VS, FS, and ash) and a response variable (GCV_E) by fitting a linear equation to the observed data. Every value of the independent variable (x) is associated with a value of the dependent variable (y). The basic model for the multiple linear regressions for n observations is expressed in Eq. 11, where α are the regression coefficients, $i = 1, 2, 3, \dots$ and ϵ is the measure of deviation [21].

$$y_i = \alpha_0 + \alpha_1 x_{i1} + \alpha_2 x_{i2} + \dots + \alpha_k x_{ik} + \epsilon_i \quad (11)$$

Relationship between the variables is then plotted to identify the trend that has the best fit. The best fitted trend is selected based on the minimum value of the sum of squares of deviation of the various data points from the line obtained. The best possible values of the regression coefficients in the equation are determined by the method of least squares. Regression equations obtained in this analysis were compared on the basis of coefficient of multiple determinations (R^2), which was calculated by Eq. 12. R^2 is a comprehensive parameter to quantify the accuracy of the equation. R^2 is such that $0 < R^2 < 1$, and denotes the strength of the linear association between x and y. An equation with a higher R^2 value makes a better prediction.

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2} \quad (12)$$

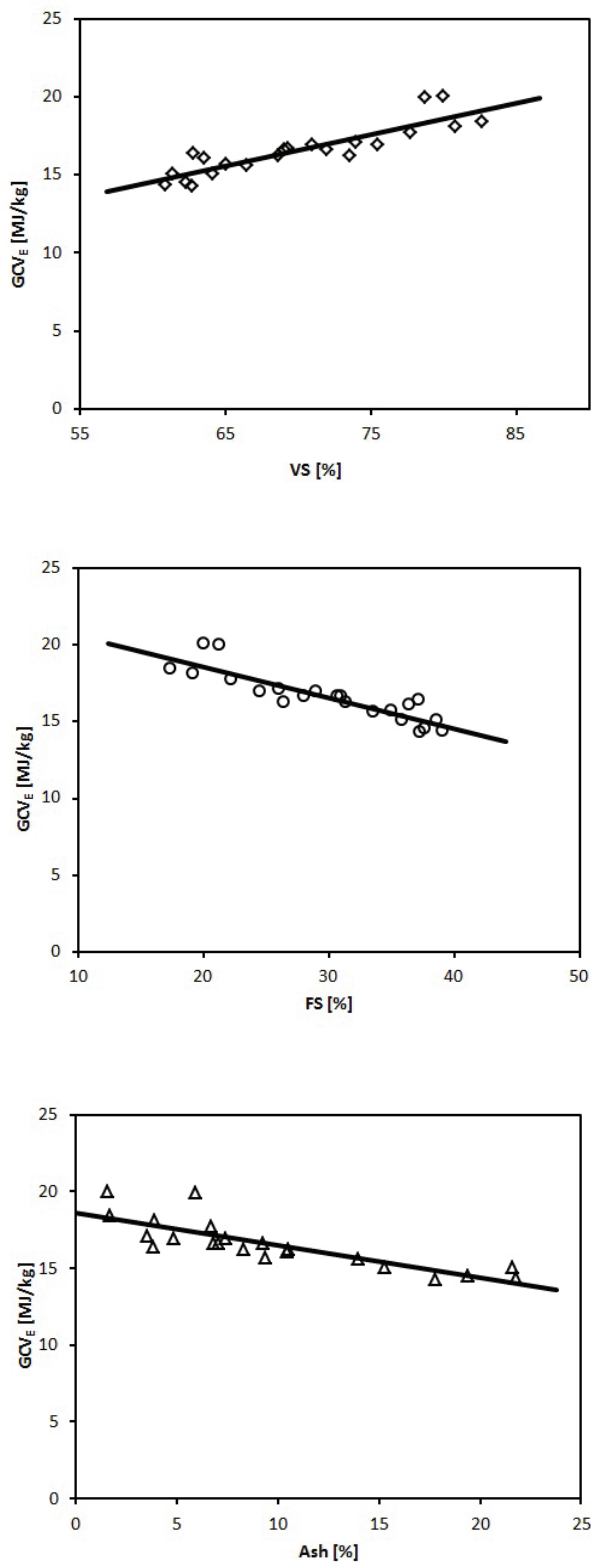


Figure 3. Effect of VS, FS and ash content on GCV_E of lignocellulosic biomass

Before developing the equations, the GCV_E was plotted as a function of VS, FS and ash as shown in Fig. 3. It indicates that all the three variables have almost linear relation with the GCV_E. Considering this qualitative relation two generalized equations Eqs. 13 and 14 were established without ash content and with ash content respectively, where x_1 , x_2 and x_3 are the values of VS, FS and ash and y is the gross calorific value computed (GCV_C) of lignocellulosic biomass. Developed GCV empirical equations and their statistical analysis are given in Table 3.

$$y = \alpha_1 x_1 + \alpha_2 x_2 \quad (13)$$

$$y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 \quad (14)$$

Moreover two statistical factors were used to assess the newly developed equations. The first was the mean absolute error (MAE) Eq. 15, and the second was the mean bias error (MBE) Eq. 16. Indeed MAE measures the closeness of GCV_C over GCV_E. The lower MAE shows higher accuracy of an empirical equation. On the other hand, if the value of MBE is positive, it shows the overestimation, while a negative value shows underestimation of an empirical equation. Sheng and Azevedo [14] reported that the smaller the MAE, the smaller the MBE of the empirical equation. The above two factors are fundamental statistical criteria widely used in the error analysis, and also have been used to assess the GCV and NCV correlations [14, 16, 22-24].

$$MAE = \frac{1}{n} \sum_{i=1}^n \left| \frac{GCV_C - GCV_E}{GCV_E} \right| \times 100 \quad (15)$$

$$MBE = \frac{1}{n} \sum_{i=1}^n \left[\frac{GCV_C - GCV_E}{GCV_E} \right] \times 100 \quad (16)$$

3. Results and Discussion

The new developed empirical equations and their statistical analysis for predicting GCV of lignocellulosic biomass are given in Table 3. The regression analysis yields Eqs. 17 and 18. It can be observed that all the constants in Eqs. 13 and 14 have positive values showing their positive effects on the GCV except β_3 , which has negative value showing the negative effect of the ash on the GCV. In addition to above, value of R^2 for Eqs. 17 and 18 are 0.783 and 0.822 respectively, which shows their significant accuracy. Eq. 18 has the lower MAE and MBE of 2.71 % and 0.13 % respectively as compared to Eq. 17, which has MAE and MBE of 3.36 % and 0.17 %. It indicates that the Eq. 18 is more accurate than Eq. 17. Moreover, referring to Fig. 4, the Eqs. 17 and 18 are more accurate than the equations based on the proximate analysis (Eqs. 1 to 8) by judging their MAEs and MBEs.

Table 3. Developed GCV empirical equations and their statistical analysis

Eq. No.	Empirical Equation	Unit	R ²	MAE [%]	MBE [%]
Eq. 17	$GCV_c = 0.22551 (VS) + 0.02505 (FS)$	MJ/kg	0.783	3.36	0.17
Eq. 18	$GCV_c = 0.21575 (VS) + 0.07492 (FS) - 0.08426 (ash)$	MJ/kg	0.822	2.71	0.13

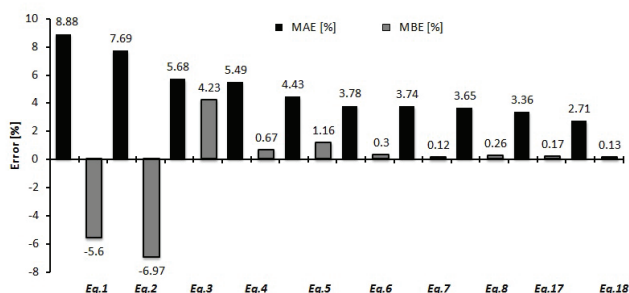


Figure 4. Comparison between MAEs and MBEs of different equations based on proximate analysis (Eqs. 1-8) and VS, FS basis (Eqs. 17 and 18)

The graphs between GCV_c and GCV_E are plotted and shown in Fig. 5, which indicates that most of the plotted values are close to the linear trend line between the GCV_c and GCV_E . The R^2 value by using Eq. 17 is 0.783, whereas by using Eq. 18 it is 0.822, confirming accuracy of later over earlier. This is because of considering ash content in Eq. 18. On contrary, determination of ash content of biomass consumes more energy, time and effort, thus increases the cost of analysis.

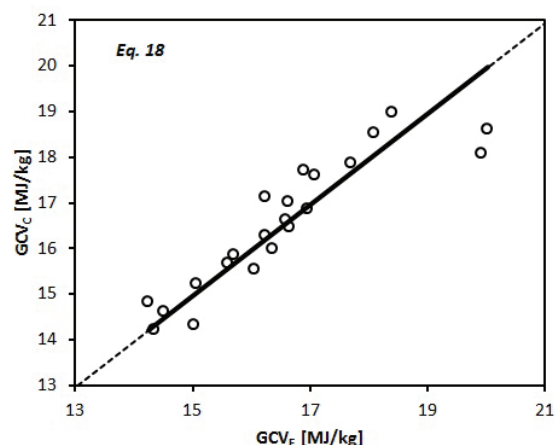
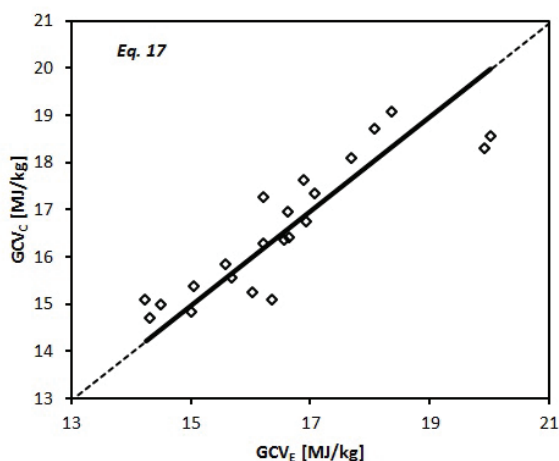


Figure 5. Graphs between GCV_E and GCV_C for Eqs. 17 and 18

4. Conclusion

Two new most simple empirical equations have been developed, which allow predicting the gross calorific value (GCV) of lignocellulosic biomass by linear regression analysis on the bases of VS, FS and with and without ash contents in the specified range of VS (60.84–82.64 %), FS (17.36–39.16 %) and ash (1.59–21.76 %) as percentage dry mass basis. In comparison with the GCV_E , the MAEs of these equations are 3.36 % and 2.71 %, and the MBEs are 0.17 % and 0.13 % without and with ash contents respectively, which are lower than the equations based on the proximate analysis available in the published literature. These equations are very useful in prediction of GCV of lignocellulosic biomass without access to the more expensive and sophisticated equipment. This method is not only easy, cost-effective and time saving alternative to estimate GCV of the lignocellulosic biomass but is also useful to measure of organic content in it, thus gives two fold benefits.

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References

- [1] Werther J, Saenger M, Hartge EU, Ogada T, Siagi Z. Combustion of agricultural residues. *Prog Energy Combust Sci* 2000;26:1–27.
- [2] Sami M, Annamalai K, Wooldridge M. Co-firing of coal and biomass fuel blends, *Prog Energy Combust Sci* 2001;27:171–214.
- [3] McKendry P. Energy production from biomass (part 1): overview of biomass. *Bioresour Technol* 2002;83:37–46.
- [4] Hall DO, Rosillo-Calle F, de Groot P. Biomass energy lessons from case studies in developing countries. *Energy Policy* 1992;62–73.
- [5] McGowan F. Controlling the greenhouse effect: the role of renewables. *Energy Policy* 1991;111–18.
- [6] Williams A, Pourkashanian M, Jones JM. Combustion of pulverized coal and biomass. *Prog Energy Combust Sci* 2001;27(6):587–610.
- [7] Erol M, Haykiri-Acma H, Kucukbayrak S. Calorific value estimation of biomass from their proximate analyses data. *Renew Energy* 2010;35:170–3.
- [8] Jenkins BM, Baxter LL, Miles Jr TR, Miles TR. Combustion properties of biomass. *Fuel Process Technol* 1998;54:17–46.
- [9] Technical Specification CEN/TS 14918:2005, Solid biofuels—method for the determination of calorific value.
- [10] Parikh J, Channiwala SA, Ghosal GK. A correlation for calculating HHV from proximate analysis of solid fuels. *Fuel* 2005;84:487–94.
- [11] Tchobanoglous G, Burton FL, Stensel HD. *Wastewater Engineering: Treatment and Reuse*. 4th ed. McGraw-Hill Companies, Inc, 2003.
- [12] Tchobanoglous G, Theisen H, Vigil S. *Integrated Solid Waste Management: Engineering Principles and Management Issues*. McGraw-Hill Tokyo, 2000.
- [13] Demirbas A. Calculation of higher heating values of biomass fuels. *Fuel* 1997;76:431–4.
- [14] Cordedo T, Marquez F, Rodriguez-Mirasol J, Rodriguez JJ. Predicting heating values of lignocellulosics and carbonaceous materials from proximate analysis. *Fuel* 2001;80:1567–71.
- [15] Yin CY. Prediction of higher heating values of biomass from proximate and ultimate analyses. *Fuel* 2011;90:1128–32.
- [16] Jimenez L, Gonzales F. Study of the physical and chemical properties of lignocellulosic residues with a view to the production of fuels. *Fuel* 1991;70:947–50.
- [17] Sheng C, Azevedo JLT. Estimating the higher heating value of biomass fuels from basic analysis data. *Biomass Bioenergy* 2005;28:499–507.
- [18] ASTM Standard E1756, 2008, “Standard Test Method for Determination of Total Solids in Biomass,” ASTM International, West Conshohocken, PA, 2008, DOI: 10.1520/E1756-08, www.astm.org.
- [19] ASTM Standard E1755, 2001 (2007), “Standard Test Method for ash in Biomass,” ASTM International, West Conshohocken, PA, 2007, DOI: 10.1520/E1755-01R07, www.astm.org.
- [20] ASTM Standard D5865, 2010ae1, “Standard Test Method for Gross Calorific Value of Coal and Coke,” ASTM International, West Conshohocken, PA, 2010, DOI: 10.1520/D5865-10AE01, www.astm.org.
- [21] Majumder AK, Jain R, Banerjee P, Barnwal JP. Development of a new proximate analysis based correlation to predict calorific value of coal. *Fuel* 2008;87:3077–81
- [22] Parikh J, Channiwala SA, Ghosal GK. A correlation for calculating elemental composition from proximate analysis of biomass materials. *Fuel* 2007;86:1710–19.
- [23] Channiwala SA, Parikh PP. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel* 2002;81:1051–63.
- [24] Shen J, Zhu S, Liu X, Zhang H, Tan J. The prediction of elemental composition of biomass based on proximate analysis. *Energy Convers Manage* 2010;51:983–7.