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Investigation on biomass briquettes as energy source in relation to their calorific values and measurement of their total carbon and elemental contents for efficient biofuel utilization

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ABSTRACT

The relationship between the high heating values (HHV's) and total elemental hydrogen and carbon contents of fourteen (14) selected biomass briquettes is studied. Analyses of the experimental results shows that, the HHV's of the biomass tested are not linearly related to their total hydrogen contents but, directly related to their total Carbon contents. HHV's calculated from emperical correlations using the elemental contents of C, H, N,S and O compared well with that of the American Standard of Testing Materials (ASTM) results and also in good agreement with the widely reported values in the acceptable range of 17-21MJ/Kg. The investigation of the effect of particle size on the HHV's indicates that finely ground particles (about 125µm) had low calorific values as the grinding resulted in a loss of some heat and made the sample vulnerable to air oxidation.

Keywords: Biomass, Briquettes, Biofuel, High Heating Value

INTRODUCTION

Fossil fuels had became the major source of global energy since the beginning of the last century. Over this time, large quantities of hydrocarbon oils, gas and coal were removed from their ground deposits (Abdullahi, et *al*, 2011). These fuels are generally used as sources of energy in transport engines, heating applications and electricity generation, and in some instances as raw-materials for the petrochemical industries. Although, the fossil fuels play a key role in the global economic and political situations, their numerous challenges accounted for a shift to a more sustainable energy sources (El Shinnawi *et al.*, 1989; Hodgson, 1999, Fabian, 2003). Environmental and ecological problems are the major issues of concern associated with exploitation of these fuels. Another major challenge with these fuels is their un-sustainability and projected depletion over the years.

The use of fuel wood in the large scale without replenishing poses serious environmental consequences in many countries, desertification being the most important one. Also population increase in countries like Nigeria places more demands on energy to light and heat homes, to cook food, to drive transport, and communication devices and provide power for industries.

To address the various energy challenges associated with non-renewable fuels, many countries have indicated commitment to biofuels production that are renewable, sustainable, cheap, efficient, safe and geographically diversified. Solid biofuels in the form of briquettes, logs, bales, chips, pellets, etc had become an important source of energy even in the rural communities. The main advantage of biofuels are its domestic origin, potential for reducing total dependence on oil and gas economy, energy security and waste management, jobs creation and source of revenues to the government and rural farmers, it also offers benefits of regional development, and social structure, especially to developing countries like Nigeria (Nigam and Singh, 2010). The bush biomass, agricultural edible and non-edible oil seeds and grains, other agricultural and industrial wastes that are largely produced daily in the country could be employed as raw-materials for both small and large scale solid and liquid biofuels production.

The determination of the calorific values and percentage of C, H, N, S and O of biofuels are important in considering their suitability as environmentally safe energy sources and their potential to produce a particular bio-energy that can be used for industrial and domestic process heat (Kumar and Pratt, 1996). Estimation of high heating value from the elemental composition of fuel is also important in performance modeling calculations on thermal system (Kumar and Pratt, 1996).

In order to provide a means of quantification of energy content of biomass, this work investigated the relationship between gross calorific values (GCV) and total hydrogen and carbon content of fourteen (14) selected plant biomass. The work also determined the key effects of particle size on the calorific values (heat value) for various biofuels samples. It was an experimentally based project and employed the used Oxygen bomb calorimeter (Parr 6100 model) and ultimate analysis in determining the calorific values of fuels either directly or indirectly. Total hydrogen contents of various biomass samples were also determined by neutron reflection technique. Comparisons between measured and calculated calorific values were made in order to see how well the empirical correlations by Boie (1952) and Channiwala and Parikh (2002) predicts experimental results.

MATERIALS AND METHODS

2.1 The Raw Materials

The raw materials used in this work are mostly plant biomass from herbaceous plants/grasses (perennial crops) and agricultural residues locally produced in Nigeria’s farmlands. These materials were collected from farmlands and local community around Mairua, Funtua, Katsina State in November 2011. They were kept under a room temperature and used in this experimental work without any pretreatment so as to represent the actual scenario (condition) by which they are used as fuel.

2.2 Sample Preparation

The samples were cut to approximately 1cm size using stainless steel scissors. The samples were sun dried and finally dried by slowly heating from 80^{o}C to 135^{o}C using electric oven held isothermally for either 2 or 5 minutes depending on the observed moisture content. This is to assured that the moisture/water content of each sample is quite negligible. The dried samples were carefully pounded in a wooden mortar with wooden pestles and then sieved to obtain 500, 212 and 125μm mesh size samples. Each powdered sample was prepared into a pellet (of about 2.5g mass) before burning in to the machine by means of a pellet press; this was done to prevent scattering of material during the combustion, with consequent incompleteness of combustion. These pellets samples were then kept in a polyethylene bags to prevent moisture absorption before experiment. The screening procedure recommended in the instrument’s manual for determining the calorific values using bomb calorimeter was observed.

2.3 Experimental Procedure and Equipments

The direct determinations of calorific values were made using a bomb calorimeter (model 6100 series manufactured by Parr Instrument Company) in the chemical engineering department, Ahmadu Bello University, Zaria. The calorific value from this machine is the high heat value (HHV), which includes the latent heat of the vapour emitted from the specimen. The machine consists of a small cup to contain the sample, an 1108 oxygen bomb with an oval bucket which fits into the insulating water jacket, a built-in semi-automatic system for charging the bomb with oxygen, high precision electronic thermometer, a bright, color, touch screen display for data entry and operation control, Special communication ports for printer, computer and network (LAN) connections, the dewar (to prevent heat flow from the calorimeter to the surroundings), ignition circuit connected to the bomb and a removable compact flash memory card slot for simple program updates and test report archiving. All steps in the test procedure are managed by a microprocessor control system programmed to operate the calorimeter in either the conventional equilibrium mode or in a faster dynamic mode. All data are handled automatically by a dedicated microcomputer. Electrical energy is used to ignite 0.025g of the fuel; as the fuel was burning, it heated up the surrounding air, which expanded and escaped through a tube that lead the air out of the calorimeter. When the air was escaping through the copper tube it also heated up the water outside the tube. The temperature of the water allowed for calculating calorie content of the fuel. Figure 1 shows the test assembly of the model Bomb calorimeter, oxygen bomb with an oval bucket used in this work.

Total hydrogen contents of the fourteen samples were determined using 1Ci ^{241}Am-Be neutron reflection facility at Centre for Energy Research and Training (CERT), Zaria. The percentage of carbon, hydrogen, nitrogen and sulfur were determined analytically while the percentage of oxygen was obtained from the subtraction of the ultimate analysis result from 100: i.e.

$$\% \text{ Oxygen} = 100 - (\%C + \%H + \%N + \%S_{organic}) \quad (1)$$

The ash content was measured according to ASTM standard as follows: A prescribed amount of sample (2 g) was weighed in a ceramic crucible and was placed in an electric muffle furnace. Because the alkali oxides are volatile at high temperatures, the temperature was kept at 550°C in the determination of ash for all samples. After 3h, the furnace was turned off and was allowed to cool down. The crucible containing the ash was weighed and the ash content of each sample was determined by difference.

$$HHV = x_1 C + x_2 H - x_3 S - x_4 N + x_5 O + x_6 A \quad (2)$$

where the coefficients $x_1 - x_6$ were determined using regression analysis with SPSS (version 15.0) for windows. The correlation relation has the R-square value of 89.1%.

The indirect determination of high heating value (HHV) of biofuels samples were made from their ultimate analysis results and total ash contents using the equations developed by Channiwala and Parikh (2002) and that of Boie's (1953) given by equations 3 and 4 respectively. The correlation between higher heating values and chemical composition was modelled as

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A \quad (3)$$

$$HHV = 0.3517C + 1.1626H + 0.1047S + 0.0628N - 0.111O \text{ MJ/Kg} \quad (4)$$

where C, H, O, N and A in equation 2.0 or 3.0, represents carbon, hydrogen, oxygen, nitrogen, sulfur and ash contents of materials expressed in mass percentage on dry basis.

The above correlations make it possible to accurately predict the gross heating values of most biomass fuels of known ultimate composition and ash content (Annamalai and Ramalingam, 1987; Chaniwala and Parikh, (2002).

RESULTS AND DISCUSSION

3.1 Ultimate Analysis and Calculated High Heat Values of the Biomass Samples

The results of elementary and ash analyses for the fourteen samples are listed in table 1.0. A good estimate of high heating value of the fuels was obtained using their ultimate analysis results.

The carbon and oxygen content is important in biomass energy analysis. High Oxygen content tends to lower the calorific value while high carbon content tends to form high-grade biomass fuel. It is evident from table 1.0 that high carbon contents contributes to the heating value positively and high oxygen content contributes negatively. It is therefore important in biomass conversion routes to de-oxidize the biomass in order to increase the heating value.

Table 1.0: Ultimate Analysis (% mass, dry basis) of Plant Biomass Samples

Fuel Name	C%	H%	S%	N%	O%	ASH%	HHV (MJ/kg) Boie's equation
Cocoanut Shells	40.23	2.483724	0.0151	0.88	56.39118	2.30	11.07972
Groundnut Shells	55.41	4.147285	0.0136	3.50	36.92912	5.00	20.25492
Coffee weed	53.75	5.399728	0.0196	1.05	39.78067	10.0	20.78842
Coffeesenna	35.92	6.101802	0.0151	3.15	54.81310	8.50	13.83635
Rice Husks	64.50	3.78208	0.0121	2.10	29.60582	20.0	23.45964
Bagasse	45.21	4.937537	0.0106	0.88	48.96186	3.00	16.46253
Maize Cobs	54.16	3.410899	0.0121	1.75	40.66700	10.0	18.48514
Rice Straw	39.26	2.946141	0.0181	2.10	55.67576	17.0	11.03164
Cotton Stalks	38.00	3.446135	0.0272	1.75	56.77667	5.00	11.32648
Sawdust	46.12	4.631472	0.0242	0.70	48.52433	5.00	16.42670
Flamboyant	61.94	5.861505	0.0302	1.58	30.58830	3.50	25.27236
Maize Husks	75.98	3.386915	0.109	2.1	18.42409	12.0	28.33641
Corn Stalks	55.61	4.622949	0.021	1.23	38.51605	37.5	20.07040
Switch Grass	75.13	3.425569	0.0181	1.93	14.49633	5.00	28.91979

The measured percentage H, N and S contents are generally much lower to that of hydrocarbon fuels and oxygen content is high to that of hydrocarbon. The total nitrogen varies in the range 0.88-3.50 (wt %) and the total sulfur range 0.0106-0.1090 (wt %). Both nitrogen and sulfur content are not important in biomass combustion. They tend to increase the release of toxic gases that are either irritants (NO_x, SO_2, aldehydes and acrolein) or asphyxiants (HCN) which may cause adverse effect to living organisms.

3.2 Effect of Particle Size on the High Heating Values of the Samples

The effect of particle size on the measured heating values of biomasses is presented in table 2 and figure 1 represent the bar chart of the results. It can be seen by comparison of the three mesh sizes; those bigger sizes (500µm and 212µm) have high calorific values than smaller (125µm) mesh size. The fine size (125µm) gives the smallest heating values in all the samples except for Flamboyant. The fine grinding resulted in a loss of some heat and made the sample vulnerable to air oxidation. This result agrees with that obtained by Kumar and Pratt (1996) when the effect of particle size on three plant biomass was analyzed.

It was observed that the measured heating values for all sizes are generally high when compared with the widely reported values in the range 17-21 MJ/kg for biomass materials. In all the sizes, 125 µm gives a better result that can be comparable to what is known in the literature. About ten data points (out of fourteen) are within the acceptable range of 17-21MJ/kg. The overestimation of high heating values in most of the data points might be due to compression force of 15 tons (15, 000Kg) that was applied in pelletizing (as the densification of the biomass increase its calorific value) or might be due to experimental condition.

The calculated higher heating values were correlated as a function of their ultimate analysis results for all sizes and the following empirical correlations were obtained from regression analysis: For 500 µm,

$$HHVs = 242.4535 - 1.8546C - 6.8718H - 122.2782S - 2.0293O - 1.9511A \tag{5}$$

With R-Squared = 0.5182. For 212 µm,

$$HHVs = 48.6348 - 0.1678C + 1.6773H + 84.7598S - 0.3239O - 0.6963A \tag{6}$$

With R-squared = 0.1998 and for 125 µm,

$$HHVs = 4.8386C + 7.2062H - 25.6657S + 4.5627O + 4.8417A - 454.744 \tag{7}$$

With R-Squared = 0.3734.

These equations, obtained from regression analysis by using the measured HHVs values as a function of their ultimate analysis results, shows that a better high heating values for biomass is obtainable with a larger particle size of 500 µm followed by 125 µm and 212 µm gives the least R-square value. These results imply that there should be certain size of the biomass that will give an optimum higher heating value.

Table 2: Effect of Particle Size on HHVs Values of the Samples

Fuel Name	HHV (MJ/kg) (500 µm)	HHV (MJ/kg) (212 µm)	HHV (MJ/kg) (125 µm)
Cocoanut Shells	23.5636	18.73625	16.12275
Groundnut Shells	38.42588	51.8665	17.6236
Coffee weed (Senna Obtusifolia)	24.92278	41.49233	12.43788
Coffee Senna (Senna Occidentalis)	14.54073	17.07803	13.95463
Rice Husks	43.3076	9.403375	8.948675
Bagasse	30.5653	33.66293	30.31925
Maize Cobs	40.095	37.39783	25.34218
Rice Straw	40.105	33.9892	9.153075
Cotton Stalks	30.96895	26.33613	16.1025
Sawdust	29.39965	37.58613	21.1178
Flamboyant	19.08298	42.1115	32.26325
Maize Husks	29.39965	39.21535	21.1178
Corn Stalks	23.99553	34.8391	45.3495
Switch Grass	30.49055	29.02033	27.8379

3.3 Relationship between High Heating Value (HHV) and Total Hydrogen/Carbon Contents (%wt) of the Samples

The percentage hydrogen contents, total carbon and high heating values for the fourteen plant samples are presented in table 1. The high heating value given in the table is estimated from equation 4.

A graph of high heating value against total hydrogen and carbon contents is plotted. From the data shown in table 1.0 and the trend of data plotted in figure 2 and 3, it is evident that the higher heating values of the fourteen selected samples is not linearly related to their total hydrogen contents but directly related to their total carbon content, i.e. the higher the carbon content of plant biomass, the higher the heat energy to do a useful work. The co-efficient R^2, which represent the correlation between HHVs and total hydrogen and carbon contents were calculated as 0.001278 and 0.931541 respectively. These calculated values show that the relationship between HHVs and total carbon contents is positive/direct while for hydrogen content there is no correlation. These results are in good agreement with the theoretical equations derived by Tillman (1978), Yin (2011), Boie (1953) and Channiwala and Parikh (2002) that the high heating value of biomass materials is a very strong function of its fixed carbon content. The fixed carbon content is defined as the material remaining after the determination of moisture, volatile matter and ash - i.e. a measure of the solid combustible material in the fuel after the expulsion of volatile matter.

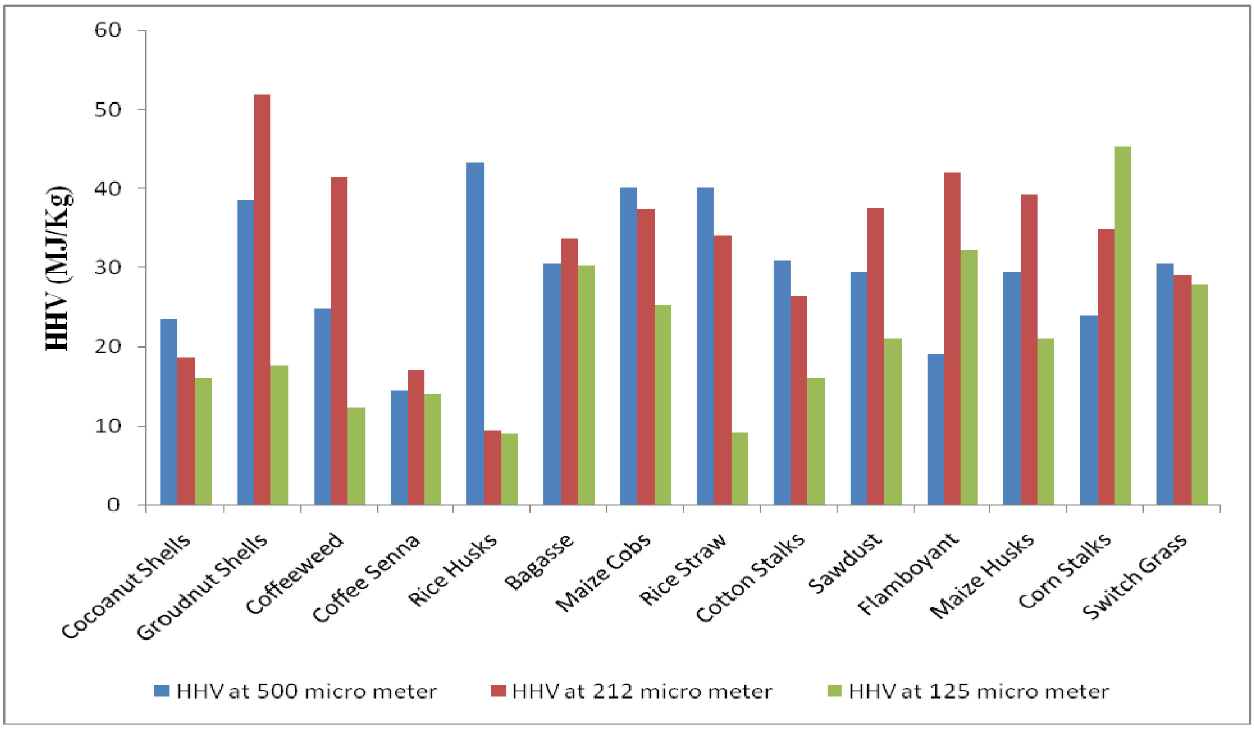

Figure 1: Effect of Particle Size on the High Heating Value

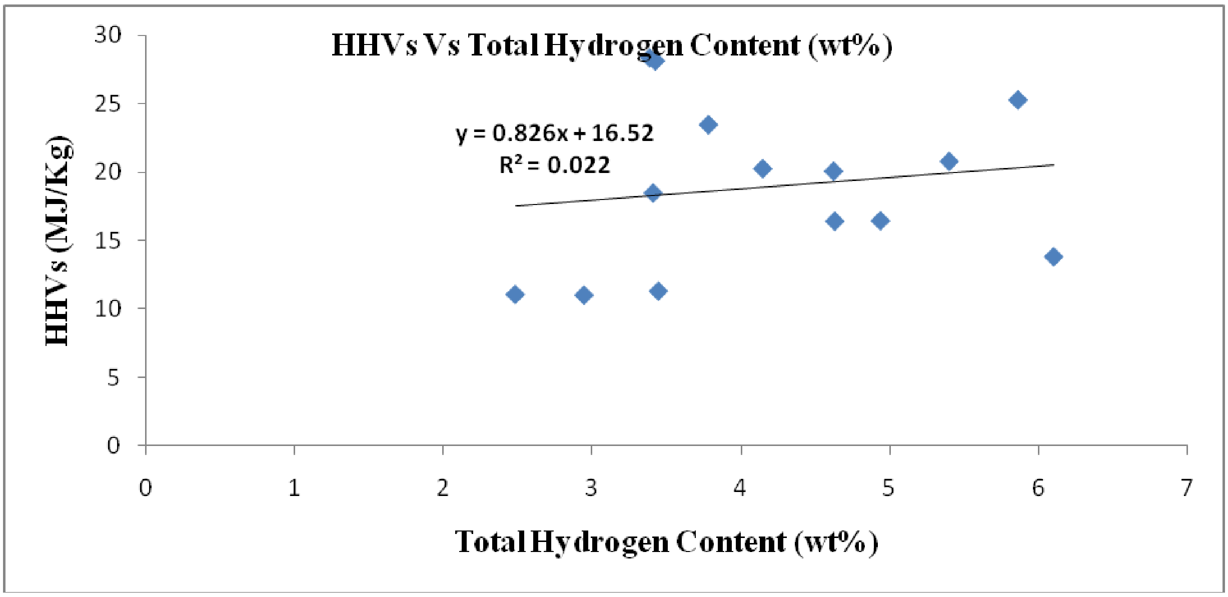

Figure 2: HHVs Against Total Hydrogen Content (%wt)

3.3: Comparison between Measured and Calculated HHVs (dry basis) of Biomass Fuels

The higher heating value (HHV) of biomass is most precisely determined by using a bomb Calorimeter, as defined for example in the British Standard Methods (BS: 1016: part 5: 1977). The calorific value from bomb machine is the high heat value (HHV), which includes the latent heat of the vapor emitted from the specimen. Higher heating value can also be estimated from empirical correlations, for example equation 3 and 4.

Table 3 shows the HHV for the measured as well as using equation 3, 4, and 5. Analysis of the results presented in this table showed that measured heating values do not excellently agreed with the modeled values as well as the calculated values estimated using empirical equations derived by Channiwala and Parikh (2002) and Boie (1953). The calculated results are considered to be more accurate in this work due to the fact that the results of the two empirical equations fairly matched and are in good agreement with widely reported HHVs in the range of 17-21MJ/Kg. Bomb measurements over predicts HHVs for a number of data points and some few data points matched the computed results. The over prediction might be due to densification of the powdered samples during preparation of biomass or might be due to experimental condition. The modeled HHVs obtained by plotting a graph of measured HHVs as a function of their ultimate analysis results computed using SPSS software.

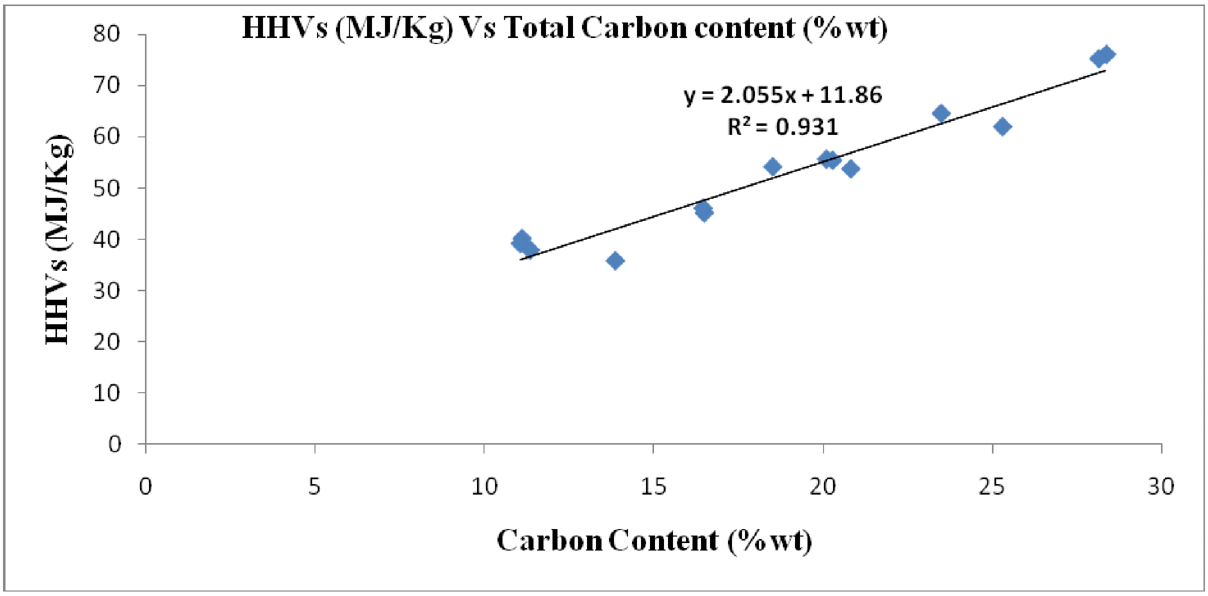

Figure 3: HHVs Against Total Carbon Content (%wt)

Table 3: Comparison between Measured and Calculated HHVs of Biomass Fuels

Fuel Name	HHV (MJ/kg) (Measured)(125µm)	Modeled HHV (MJ/kg)	HHV (MJ/kg) Boie's equation	HHV(MJ/kg) (Channiwala & Parikh's equat.)	ASTM (MJ/kg)
Cocoanut Shells	16.1228	15.34114	10.83389	11.07972	-
Groundnut Shells	17.6236	12.77548	20.43142	20.25492	20.18
Coffeeweed (Senna Obtusifolia)	12.4379	28.01931	20.83394	20.78842	-
Coffee senna (Senna Occidentalis)	13.9546	15.09184	13.84217	13.83635	-
Rice Husks	8.94868	24.93586	23.9286	23.45964	-
Bagasse	30.3193	23.53483	16.26234	16.46253	17.33
Maize Cobs	25.3422	19.90732	18.61071	18.48514	-
Rice Straw	9.15308	14.74103	11.18669	11.03164	16.28
Cotton Stalks	16.1025	13.68888	11.18161	11.32648	15.22
Sawdust	21.1178	23.94481	16.26525	16.4267	16.23
Flamboyant	32.26325	26.94891	25.30597	25.27236	-
Maize Husks	21.1178	21.89843	28.75801	28.33641	-
Corn Stalks	45.3495	33.28789	20.73684	20.0704	-
Switch Grass	27.8379	23.33630	28.36479	28.11549	

CONCLUSION

A bomb calorimeter (Parr 6100) was used to measure directly the high heating values of the fourteen selected plant biomass. Elemental C, N, S and ash were determined analytically and Oxygen (O) by subtraction. A non destructive technique based on the neutron reflection technique was used to determined total hydrogen (H) contents from the samples. Analysis of the experimental data confirmed the following:

1. HHVs of the fourteen biomass tested are not a function of their total hydrogen contents but a function of their total carbon contents. The co-efficient R^2, which represent the correlation between HHVs and total hydrogen and carbon contents were calculated as 0.001278 and 0.931541 respectively.
2. The measured elemental H, N and S contents are generally much lower to that of fossil fuels but oxygen content is high to that of fossil fuels. The total nitrogen measured varies in the range 0.88-3.50 (wt %) and the total sulphur range 0.0106-0.1090 (wt %).
3. Comparisons of the measured (Bomb measurements) and calculated results showed that measured heating values do not excellently agreed with the calculated values estimated using empirical equations derived by Channiwala and Parikh (2001) and Boie (1953). The calculated results are considered to be more accurate in this work due to the fact that the results of the two empirical equations fairly matched and are in good agreement with widely reported HHVs in the range of 17-21MJ/Kg.
4. The biomass particle size in the biofuels preparation has serious effect on the high heating values of the samples. Finely ground particle (with larger surface area, 125μm) tend to loss some heat and made the sample vulnerable to air oxidation and therefore gives low HHVs.

It is however recommended that the relationship between the HHVs and total hydrogen/carbon content of some other plant biomass should be investigated so as to confirm if a general statement can be drawn regarding the combustion relationship between biomass HHV and its total carbon or hydrogen content. There is also need to repeat the experiment with the bomb machine for some other plants biomass in order to verify the major disagreement between the measured and calculated HHVs of biomass.

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