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INTER-RELATIONSHIPS BETWEEN HYDROGEN AND CARBON CONTENTS OF BIOMASS FUELS AND THE CALORIFIC VALUES

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ABSTRACT

Empirical relationships between hydrogen and carbon contents and the calorific values of rice husks, cotton seeds, jatropha seeds, palm kernel shells and cashew shells were investigated. The experimental data indicated higher correlation coefficient between calorific value and hydrogen content than between calorific value and carbon content, as compared with Tillman predictions. Therefore, the calorific values can be estimated based on hydrogen content of the biomass fuel.

1. INTRODUCTION

Under the current worldwide energy crisis, renewable energy is a solution that can also address environmental issues, and nations must opt for green energy, such as biomass, solar and wind. If combusted efficiently, biomass as renewable energy source can reduce substantially the net emissions of greenhouse gases at economically acceptable costs.

In Benin, biomass is the main domestic energy resource, constituting about 49.5 % of total domestic energy requirements [1]. The establishment of new agro-industries processing agricultural products has increased the total amount of agro-industrial wastes produced, which must be exploited efficiently to generate energy to reduce the country's dependence on conventional energy.

However, the contribution of biomass to the energy-mix requires adequate knowledge of the physico-chemical characteristics of the biofuels [2, 3]. Specifically, the calorific values are required in order to determine the appropriate optimal conversion methods of the biomass energy. The peculiarities of renewable energy sourcing and conversion systems in developing countries demand that local research be conducted to evaluate the biofuels, instead of depending on data from other sources, which might decrease the effectiveness of biomass energy conversion.

In this paper, experimental assessment of hydrogen and carbon contents of plant-based biofuels (rice husks, cotton seeds, palm kernel shells, jatropha seeds and cashew shells) in relation to the calorific values are presented. In addition, semi-empirical mathematical relations between the calorific values and hydrogen and carbon contents were established.

2. SELECTION OF BIOMASS FUELS

The common plant materials in Benin are rice (*Oryza glaberrima*) husks, cotton (*Gossypium hirsutum*) seeds, cashew (*Arnacardium occidental*) shells, jatropha (*Jatropha curcas*) seeds and palm kernel (*Elaeisis guineensis*) shells, which can be converted into biofuels were selected to determine the inter-relationships between hydrogen and carbon contents and the calorific values.

The estimated exploitable biomass residues per year are 1000 tons of cashew shells, 10000 tons of rice husks and 88000 tons of cotton seeds. The biofuels were obtained from the food processing industries, in particular, the rice mills and cashew shelling factories.

The dependence of calorific values or fuel contents on elemental compositions of some biomass have been reported by Amy (hydrogen, carbon and oxygen) [4] and Tilman (carbon) [5], but excluded the biofuels listed for the present research.

3. EXPERIMENTAL WORK

3.1. Moisture Content and Density

The moisture content (X %) of the raw biomass was determined on wet basis, using the equation,

$$X(\%) = \frac{M_1 - M_2}{M_1} \times 100 \qquad (1)$$

where M_1 was as-received mass, and M_2 was constant mass attained after drying in an oven at 110 °C for 2 hours [6].

The density of as-received biomass was determined by ratio of the mass to the displaced volume in water.

3.2. Elemental Hydrogen (H) and Carbon (C) Analysis

The carbon content was determined by Anne method [7], where the organic carbon was oxidized by potassium biochromate in sulphuric acid solution. The chemical reaction was

$2K_2Cr_2O_7 + 8H_2SO_4 + 3C \longrightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 3CO_2 + 8H_2O$ (1)

The quantity of dichromate in excess was reduced proportionally to the organic carbon content. The excess dichromate was quantified by a solution of Mohr Salt in the presence of diphenylamine to an accuracy of ± 1 %.

The hydrogen content was determined by mass spectroscopy, using Energy Dispersive Spectroscopy Model SEM-EDS/FEI/XL40 TMP/ESEM at COFRAC (ISO17025) accredited Laboratory of SOCOR [8].

3.3. Calorific Value (CV) J/kg

The CV was determined by bomb calorimeter (KA Calorimeter System C7000). The water temperature in the calorimeter was increased by burning a certain quantity of biomass fuel in oxygen atmosphere at ambient conditions [9], and the CV was calculated from the temperature rise of the water. Account was taken of the heat released in the ignition fuse, thermal corrections, thermochemistry, and heat absorbed by the calorimeter water jacket.

Under optimum settings and conditions, the C7000 calorimeter achieved measurement reproducibility of ± 0.2 % (DIN 51900), guaranteed under the set up shown in Table 1 for both calibration and measurements.

The C7000 calorimeter was designed for an energy input of up to 30 kJ, and operated reliably in ambient temperatures between 18 and 30 °C. For accurate measurements, temperature variations were minimized. The calibration was carried out by burning a known quantity of a reference substance (benzoic acid) in the decomposition vessel under test conditions. Since the CV of the reference substance was known, the temperature increase of the decomposition vessel was used to calculate the heat capacity.

Table 1. C7000 operational settings

Criterion	Value
Calibration substance	Benzoic acid (C_6H_5COOH)
Sample mass	1.00 ± 0.05 g
Ambient temperature	25 ± 1 °C
Temperature of decomposition vessel before determination	25 ± 1 °C
Oxygen pressure	30 bar
Measurement period max. (pre- and main test)	7.2 min

The CV was calculated using the equation [9],

$$CV = \frac{(\Delta\theta) \times \bar{C}_s - e_1 - e_2 - e_3 - e_4}{M_f} \quad (2)$$

where $\Delta\theta$ is corrected change in temperature for the difference between ignition temperature and final temperature after complete combustion, $\bar{C}_s$ is mean effective heat capacity of the calorimeter (J/K) (determined by 5 trials), e_1 is correction for heat of combustion of cotton (J), e_2 is correction for heat of combustion of the ignition wire (J), e_3 is correction for heat resulting from the formation of sulphuric acid (J), e_4 is correction for heat resulting from the formation of nitric acid (J) and M_f is mass of the biofuel sample (kg)

4. RESULTS

4.1. Experimental Data

Table 2 is a summary of the data on moisture content, density, carbon and hydrogen contents, and CV obtained for the different biomasses considered.

Table 2. Physico-chemical data and characteristics of the biomass

Biofuel	Moisture Content X (%)	Density kg/m^3	Carbon Content $\times 10^2$ ppm	Hydrogen Content $\times 10^2$ ppm	Calorific Value CV (MJ/kg)
Rice husks	12.4	128.0	476.40	5.10	14.671
Cotton seeds	9.6	410.0	595.20	5.93	18.874
Jatropha seeds	11.8	250.0	633.60	6.79	22.140
Cashew shells	14.1	481.8	714.00	7.20	23.308
Palm kernel shells	10.3	640.0	748.80	8.73	26.917

4.2. Relationship between CV and C content

The correlation between the CV and C content established independent of the hydrogen content of the biomass is shown in Fig. 1, plotted using data from Table 2 and compared with Tillman data. The linear regression or the trend equation was of the form,

$$CV = 0.508C - 5.637 \text{ (MJ/kg)} \quad (3)$$

with linear correlation coefficient, $r^2 = 0.9562$.

4.3. Relationship between CV and H content

Using data from Table 2, Fig. 2 was plotted to show the correlation between CV and hydrogen content of the biomass (independent of C content) with trend or linear regression equation of the form,

$$CV = 3.323 H - 1.247 \text{ (MJ/ kg)} \quad (4)$$

with linear correlation coefficient, $r^2 = 0.9649$.

4.4. Inter-Relationship between CV, H and C contents

From the experimental data, and adopting the trial-and-errors procedure [10], the relationship between CV, H and C content was established as,

$$CV= 0.253C + 1.661H - 3.442 \quad (5)$$

The experimental values and predicted values using eqn. (5) are also shown in Table 3, where the % error is the difference between the two sets of data

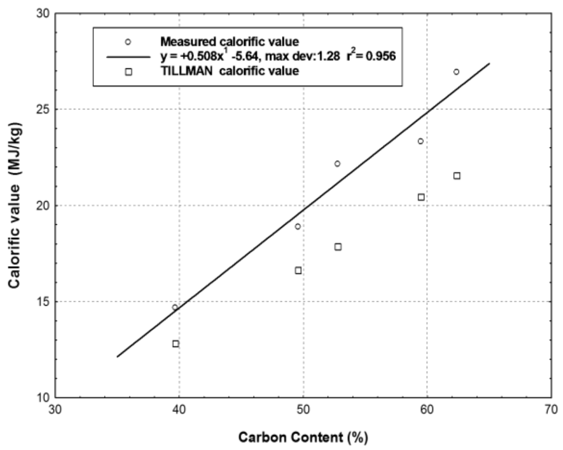

Fig 1. CV (MJ kg) based on carbon content

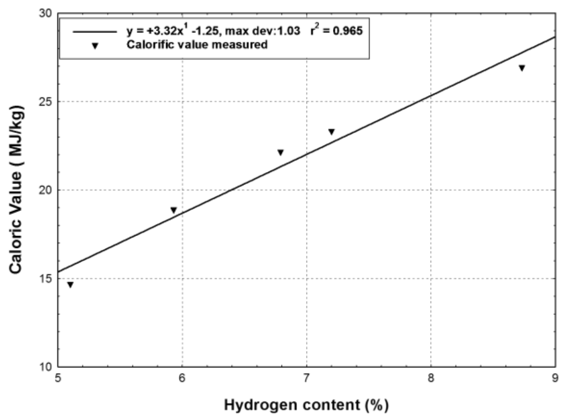

Fig 2. CV (MJ/kg) based on hydrogen content

Table 3. Experimental and Predicted CV values

Biomass	% C	% H	CV Measured (MJ/kg)	CV Predicted (MJ/kg)	% Error
Rice husks	39.7	5.10	14.671	15.073	2.7
Cotton seeds	49.6	5.93	18.874	18.956	0,4
Jatropha seeds	52.8	6.79	22.140	21.194	4.3
Cashew shells	59.5	7.20	23.140	23.570	1.9
Palm kernel shells	62.4	8.73	26.917	26.845	0.3

5. DISCUSSION

Of all the physico-chemical characteristics of biomass fuels, the calorific value is the most important parameter for biomass energy recovery. The data showed strong linkage between carbon and hydrogen contents and calorific values.

According to Amy [4], the calorific value was given by

$$CV=34.03C+121.64H-12.54O \text{ MJ/kg} \quad (6)$$

where O is oxygen content, but according to Tillman [5], the calorific value and carbon content were related by expression,

$$CV = 0.385C - 2.475 \text{ (MJ/kg)} \quad (7)$$

Table 4 shows data comparison between the experimental values and calculated values by Tillman equation and eqn. (3). Equation (3) gave values close to the measured CVs, when compared with Tillman eqn. (7).

The graph in Fig. 3 shows the differences between the regression eqn. (3), experimental values and Tillman equation. Therefore, the eqn. (3) obtained from the study is suitable to describe the relationship between calorific value and carbon content of agricultural biomass.

Table 4. Comparison of Experimental and Calculated calorific values

Biomass	**Experimental/Measured** Calorific Value **(MJ/kg)**	**Estimated** Calorific Value **(MJ/kg)**	**Tillman** Calorific Value **(MJ/kg)**	**Tillman Difference %**	**Equation Difference %**
Rice husks	14.671	14.528	12.809	12.688	0.974
Cottonseed	18.874	19.556	16.621	11.937	- 3.616
Jatropha	22.140	21.182	17.853	19.363	4.327
Mahogany shells	23.308	24.585	20.432	12.339	- 5.479
Palm kernel	26.917	26.058	21.549	19.943	3.190

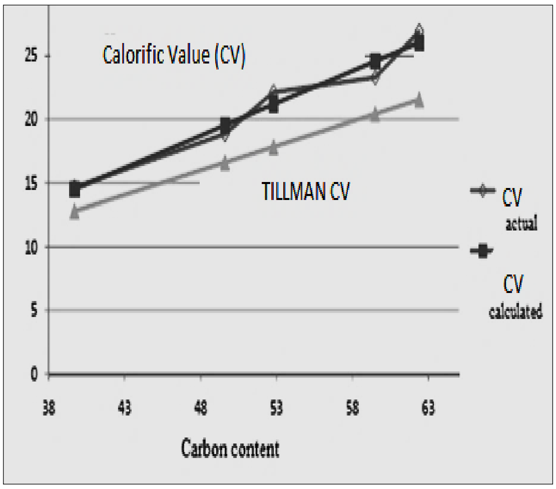

Fig 3. Calorific value (MJ/kg) based on carbon content.

6. CONCLUSIONS

Experimental calorific values were determined by calorimetry and the data were fitted by trend equations to predict the values based on either H or C content.

The inter-relationships between calorific value and hydrogen and carbon contents of biomass were established by linear regression analysis. The calorific values could be calculated based on the hydrogen content of the biomass, as the correlation with hydrogen content provided accurate data.

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