

Original Research Paper

# Assessment of Efficient Thermal Conversion Technologies and HHV from Compositional Characteristics of Cassava Peelings, Plantain Peelings and Corn Cobs

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**Abstract:** The understanding of compositional characteristics permits to predict the efficient thermal conversion technologies and Higher Heating Value (HHV). Although HHV can be determined directly, many models have been proposed for HHV prediction. They are based on proximate, ultimate, and structural analysis and require much data collected. The present work assesses to predict efficient thermal conversion technologies and HHV of the most abundant agricultural biomass from Cameroon, namely cassava peelings, plantain peelings, and corn cobs, by using the existing models and exploring the calculation of HHV from the formula. The results show that investigated biomasses can be efficiently used in thermochemical conversion to produce bio-oil/syngas, in the biochemical process to produce bioethanol/biogas, and in the physical process to densify feedstock into fuel briquette. Flue gas reveals a value less than the toxic values fixed by the European standard for household waste incineration and can therefore be used as an environmentally friendly bioenergy source. Nevertheless, the levels of S and N could be taken into account in the design of a gasification plant to control the emission of NO<sub>2</sub> and SO<sub>x</sub>-derived pollutants as their value is more than the limit fixed. Amongst the existing models, the model based on ultimate analysis gives the best correlation. The Average Absolute Error (AAE) is ranging from 2.47 to 10.71%. The calculation of HHV from combustion enthalpy and the formulae of cassava peelings, plantain peelings, and corn cob are C<sub>5</sub>H<sub>4</sub>O<sub>2</sub>, C<sub>5</sub>H<sub>8</sub>O<sub>4</sub>, and C<sub>3</sub>H<sub>4</sub>O<sub>2</sub> respectively. The HHV derived from them is 16.13, 16.27, and 20.02 MJ/kg for cassava peelings, plantain peelings, and corn cob respectively. The AAE lies within 2.52 and 8.08%. These values are lower than those obtained from the literature models. These AAE varies between 4 and 10%. The AAE of the twenty biomasses from the literature ranges from 0.16 to 10.96%.

**Keywords:** Biomass Conversion, Higher Heating Value, Thermochemical Process, Biochemical Process

## Introduction

Biomass appears as a promising and affordable source of energy for less developed countries like Cameroon to solve the energy deficits observed (Liu *et al.*, 2014;

Samomssa *et al.*, 2021). However, they are many methods to convert biomass to energy and the efficient choice of conversion is related to biomass properties (Monir *et al.*, 2020). These properties are proximate, ultimate, and structural analyses and are the main

parameters needed to predict feedstock behavior during thermal conversion (Elinge *et al.*, 2019; Zhou *et al.*, 2019). Thus the latent heat of moisture content evaporation decreases heating value (Samomssa *et al.*, 2022; Wang, 2008) while, the volatile matter leads to easy ignition, fast burning, and a proportionate increase in flame length (Da Silva *et al.*, 2021). Ash content decreases heat and oxygen diffusion during combustion and higher heating value content (Akowuah *et al.*, 2012; Mohammed *et al.*, 2020). Fixed carbon generates heat during burning (Da Silva *et al.*, 2021). Carbon, hydrogen, nitrogen, sulfur, and oxygen predict the number of gases released during combustion (Buckley and Schwarz, 2003) while cellulose, hemicellulose, lignin, and extractible affect flue gases, heating value, fixed carbon and volatile matter (Sasmal *et al.*, 2012; Munir *et al.*, 2009). Hence, the understanding of these analyses allows us to predict conversion conditions (Da Silva *et al.*, 2021). Nevertheless, the literature reveals that properties of the same feedstock vary from one area to another (Samomssa *et al.*, 2019; 2015; 2021) probably due to the climate, soil, and fertilizer variations. Thus, the understanding of feedstock properties in a given area could help to predict efficient thermal conversion technologies and process parameters. In Cameroon, corn cobs, cassava, and plantain peelings are abundant biomass with the following annual productions in tons 362 509, 175 145, and 186 960 respectively (Samomssa *et al.*, 2015), and studies on their thermal properties are limited.

In addition, higher heating value is one of the most important properties of fuels which explains the energy content and determines the ultimate use of biomass and fossil fuels. Higher heating value is used to design calculations or numerical simulations of thermal conversion systems for fuels (Acar *et al.*, 2016). The common methods for determining Higher Heating Values (HHV), may be classified into two groups: Direct experimentation using a calorimetric bomb and theory by calculation from models based on proximate, ultimate and structural analysis. However, the apparatus for direct experimentation is expensive and generally not available for low-developing countries such as Cameroon. The instrument may not be accessible for theoretical researchers and engineers for modeling and feasibility studies of processes where the heating values for various biomasses are needed (Mohammed *et al.*, 2014). The calculation of the HHV is usually costly, especially in a time (of analysis) and money (of equipment) (Callejón-Ferre *et al.*, 2014).

To resolve the problem, the literature presents many models that are based on proximate analysis, ultimate analysis, and structural analysis (Demirbaş, 2001; Sheng and Azevedo, 2005; Yin, 2011). The limiting factors of these equations are that the elaboration of these models considers more than two hundred experimental data and the equations obtained are usually applied only to certain types of fuels and the ash value must belong to

a set interval (Mohammed *et al.*, 2014). Thus, the results from this equation lead to a wide variation from values reported in the literature. In addition, (Álvarez *et al.*, 2015) have observed that the fractions used to calculate HHV values may be expressed on a different basis by different authors. In recent decades, the near-infrared spectroscopic technique is more used for the prediction of higher heating values (Zhang *et al.*, 2017). The complexity of these models limits their applicability (Majumder *et al.*, 2008). However, ultimate analysis has been used to represent biomass composition by a molecular formula such as  $C_xH_yO_z$  in order to determine the nature and amount of gas releases during combustion (Chaney, 2010; Wang *et al.*, 2011; Halder *et al.*, 2014; Shen *et al.*, 2015). This molecular formula can be also used to calculate the combustion enthalpy and deduce the HHV.

The objective of this study is to predict efficient thermal conversion technologies and to explore the calculation of the HHV based on the enthalpy combustion of corn cobs, cassava, and plantain peelings from Cameroon. To achieve this goal, proximate, ultimate, and structural analyses were performed, existing models were tested and higher heating value based on enthalpy combustion was explored.

## Materials and Methods

### Sampling

The bioresources used in this study were corn cobs, plantain peelings, and cassava peelings which were collected on the field, washed several times with tap water followed by distilled water, and dried at 50°C until constant mass. Powder samples were then prepared by grinding the dried samples.

### Determination of Compositional Characteristics

#### Ultimate Analysis

Ultimate analysis was obtained using Perkin Elmer elemental analyzer according to technical standard “EN 15104:2011 Solid biofuels. (EN, 2011).”

#### Proximate Analysis

Proximate analysis of different wastes was also investigated. The moisture content was evaluated according to (ASTM, 2007; 2006a), Volatile Matter (%VM) by ASTM (2006b); ASTM (2006a) method, and ash (%ash) by ASTM (2006b) method (ASTM, 2007).

For moisture content, 1 g ( $W_1$ ) of the sample is placed in a pre-weighed crucible and dried in an oven at 105°C until constant mass and then weighed ( $W_2$ ). For ash content, the whole  $W_2$  was incinerated in a muffle furnace at 550°C for 4 h. The crucible was then transferred for cooling into a desiccator and then weighed ( $W_3$ ). The moisture content and ash content were calculated by using Eq. (1) and (2):

$$\text{Moisture Content (\%)} = \frac{w_2 - w_1}{w_1} \times 100 \quad (1)$$

$$\text{Ash Contents (\%)} = \frac{w_3 - w_1}{w_2 - w_1} \times 100 \quad (2)$$

where:

$W_1$  = Weight of the crucible,

$W_2$  = Weight of the crucible + sample before incineration and

$W_3$  = Weight of the crucible + sample after incineration

For the volatile matter, 1 g of the sample was placed in a pre-weighted crucible in an oven at 105°C until constant mass and weighed ( $m_1$ ). The dry sample in well closed was incinerated in a muffle furnace at 550°C for 10 min and then weighed ( $m_2$ ). The VM is obtained from Eq. (3):

$$\%VM = \frac{m_2 - m_1}{m_1} * 100 \quad (3)$$

where:

$m_1$  = Weight of crucible + sample after oven

$m_2$  = Weight of crucible + sample after incineration

Fixed Carbon percentage (% FC) was calculated by the following equation:

$$FC = 100 - (\%ash + \%VM) \quad (4)$$

The High Heating Value (HHV) expressed in MJ/(kg w-b) was determined using an oxygen bomb calorimeter (Parr 6100 Model A1329 DD, ID lot number M15320).

### Structural Analysis

Acid Detergent Fiber (ADF) and Neutral Detergent Fiber (NDF) were determined using the Association of Official Analytical Chemists method. Hemicellulose was obtained using Eq. 5:

$$\text{Hemicellulose} = \text{NDF} - \text{ADF} \quad (5)$$

To determine the cellulose and lignin content, the extraction/precipitation method was used. Cellulose determination consists of delignification with ethanol and nitric acid. The nitric acid causes the transformation of lignin into nitrate products, soluble in alcohol. At the same time, hemicelluloses are also hydrolyzed and ethanol protects the cellulose content. The white paste obtained is cellulose.

The lignin content consists of removing cellulose and hemicelluloses using 72% sulphuric acid. 1 g of sample was mixed with 5 mL of 72% sulphuric acid and then

placed at 30°C for 1 h. The hydrolyzed material was diluted until 4% and kept again at 30°C for 1 h. The residue was dried at 105°C until constant mass after burning in a furnace at 550°C.

### Modeling

#### Investigation of Models Based on Proximate, Ultimate, and Structural Analysis

The literature presents many models to determine higher heating value in the function of proximate analysis, ultimate analysis, and structural analysis. In this study, these models were tested on investigated wastes. Due to the large number of models presented in the literature, only the models having an average absolute error less than or equal to 25% were considered.

#### Calculation of Higher Heating Value from Combustion Enthalpy

Calculation of a higher heating value from combustion enthalpy consists of reducing the material to a chemical compound ( $C_xH_yO_z$ ) using ultimate analysis and calculating its heating value using its combustion enthalpy. Enthalpy expresses the amount of heat and mechanical work against the external pressure supplied or received by a system that transforms at constant pressure. The standard enthalpy of formation of a chemical species  $\Delta_f H^0$  is the enthalpy change corresponding to the formation reaction of this material at a constant pressure of 1 bar, at 298 K from single materials in their most stable state. The values of the enthalpies of formation of each sample were obtained from the (HCPE, 2003) solid biofuels: Determination of total content of carbon, hydrogen nitrogen, and sulfur. Instrumental methods (HCPE, 2003). Carbon, hydrogen, and oxygen were chosen because they are significantly higher in lignocellulose waste. The determination of  $x$ ,  $y$ , and  $z$  was considered to correspond to C, H, and O contents. Solving the following equations allowed us to determine  $x$ ,  $y$  and  $z$ .

For carbon:

$$\%C = \frac{12x}{M} \quad (6)$$

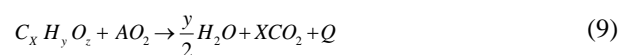
For Hydrogen:

$$\%H = \frac{y}{M} \quad (7)$$

For Oxygen:

$$\%O = \frac{16z}{M} \quad (8)$$

The combustion equation is then written:



$$X\Delta H(CO_2) + Y/2\Delta H(H_2O) - C\Delta H(CXH_3Oz) - A\Delta H(O_2) = \text{combustion enthalpy} \quad (10)$$

As a function of the combustion equation, Hess's law was used to determine the combustion enthalpy. To determine the heating value, the enthalpy of combustion of each bioresource was divided by molecular mass.

### Calculation of Flue Gases

Models were used to calculate flue gases which include the volume of CO<sub>2</sub>, SO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O (g) and O<sub>2</sub> generated, and comburivorous power (V<sub>a</sub>), smoking power (V<sub>sp</sub>) were deduced from flue gases (Jeannot, 2011). The comburivorous power represents the quantity of air containing oxygen strictly necessary and sufficient to obtain the neutral combustion of 1 kg of solid or liquid fuel or 1 m<sup>3</sup> of gaseous fuel. The smoking power is the amount of flue gas or smoke produced by the neutral combustion of 1 kg of solid or liquid fuel or 1 m<sup>3</sup> of gaseous fuel. The general equation for the calculation of these volumes is presented by the equation:

$$VX = \%X * 22.4 / MX \quad (11)$$

where, X can be C, H, O, N, or S. comburivorous Power:

$$V_a = \frac{1}{\Psi} (V_{CO_2} + V_{SO_2} + \frac{1}{2}V_{H_2O} - V_{O_2}) \quad (12)$$

Ψ is oxygen content. Dry smoking power (V<sub>dsp</sub>):

$$V_{dsp} = V_{CO_2} + V_{SO_2} + V_{N_2} + (1 - \Psi) * V_a \quad (13)$$

Wet smoking power (V<sub>wsp</sub>):

$$V_{wsp} = V_{FS} + V_{H_2O} + V_{H_2} \quad (14)$$

Carbon monoxide CO emitted was evaluated using a gas analyzer.

### Statistical Analysis

Matlab was used to calculate x, y, and z for each bioresource. The average absolute error was calculated with the following equation:

$$\text{Average absolute error \%} = \frac{HHV_{exp} - HHV_{cal}}{HHV_{exp}} * 100 \quad (15)$$

## Results and Discussion

### Analyzing Proximate, Ultimate and Structural Analyses

Table 1 presents proximate, ultimate, and structural analyses of studied bioresources. For proximate analysis, this table reveals that volatile matter is the

most important for the three bioresources with corn cobs showing the higher value. Ash content and fixed carbon are closer in cassava peelings while ash content is lower in corn cobs compared to plantain peelings. Moisture content is low for studied biomasses and a higher heating value is in the interval set to be used as fuel. Proximate analysis is the main parameter needed to predict conversion conditions (Elinge *et al.*, 2019). Volatile matter reveals the number of volatile components in the biomass like cellulose, hemicellulose, and phenol (Jeannot, 2011; Raj *et al.*, 2015). Thus, the studied biomasses present highly volatile matter and can be efficiently used in pyrolysis, gasification, and fermentation for the bioethanol process. The ash content represents the metal and inorganic compounds in biomass as phosphorous, copper, and potassium (Raj *et al.*, 2015). Hence, ash content slows down heat transfer, and oxygen diffusion to biomass surface and leads to dust emissions, and air pollution and affects the combustion volume and efficiency. The higher ash content decreases the heating value (Raj *et al.*, 2015). The ash contents in the investigated biomasses are low which reveals their propensity to be used as fuel. Fixed carbon is mostly represented by carbon which is responsible to generate heat (Jahirul *et al.*, 2012). The highest fixed carbon increases the biochar production via thermochemical processes and it is not favorable for investigated biomasses looking at their low values. Moisture content is relatively low and less than 10% thus, reveals their efficiency to be used in the thermochemical process to produce bio-oil and syngas.

Concerning ultimate analysis, Table 1 shows that oxygen is highest in cassava and plantain peelings followed by carbon content and hydrogen presents the average value while nitrogen and sulfur are the lowest. In corn cobs, carbon is higher followed by oxygen and hydrogen. Nitrogen and sulfur are also the lowest in corn cobs. Carbon content increases the heating value and fixed carbon through thermochemical conversion technologies (Monir *et al.*, 2020). Hydrogen content and carbon-hydrogen ratio contribute to increasing heating value while oxygen and nitrogen decrease heating value (Raj *et al.*, 2015). Nitrogen and oxygen contents permit the prediction of the number of gas emissions during combustion (Zhou *et al.*, 2019). Nitrogen and sulfur are the lowest value in investigated biomasses. The low fractions of nitrogen and sulfur reveal that these biomasses are more environmentally friendly than conventional fossil fuels. Nevertheless, sulfur of more than 0.1% can cause corrosion, and concentrations higher than 0.2% can emit SO<sub>x</sub> (Chico-Santamarta *et al.*, 2013).

**Table 1:** Proximate, ultimate and structural analyses of bioresources on a dry basis

Samples	Proximate analysis (%)					
	VM	Ash	FC	MC	HHV	/
Cassava peelings	84.2±2.0	8.0±0.7	7.10±1.4	7.3±0.6	15.59	/
Plantain peelings	88.2±1.3	4.7±0.7	7.80±0.7	9.3±0.3	16.69	/
Corn cob	92.5±1.0	0.8±0.3	6.80±0.8	8.2±0.3	21.78	/
Ultimate analysis (%)						
Sample	C	H	N	O	S	C/H
Cassava peelings	35.26±0.02	6.48±0.2	2.42±0.3	54.10±0.3	1.8±0.10	3.7±0.1
Plantain peelings	44.38±0.10	6.12±0.1	0.83±0.1	46.76±0.1	1.9±0.10	7.3±0.2
Corn cob	49.13±0.10	6.05±0.1	0.24±0.1	44.35±0.2	0.2±0.02	8.1±0.1
Structural analysis (%)						
Sample	Ce	He	L			
Cassava peelings	13.32±0.91	22.09±0.15	12.91±0.63			
Plantain peelings	12.73±0.55	11.09±0.57	1.83±0.14			
Corn cob	47.03±0.52	24.78±1.37	14.22±0.52			

**Table 2:** Models based on proximate analysis

Models	Samples	VM	Ash	FC	Experimental HHV value (MJ/kg)	Calculated HHV value (MJ/kg)	AAE (%)
HHV=19.610-0.242*ash.....(19) (Jenkins and Ebeling, 1985)	Cassava peelings	84.17	7.99	7.10	15.59	17.68	13.41
	Plantain peelings	88.17	4.74	7.84	16.69	18.46	10.61
	Corn cob	92.50	0.75	6.75	21.78	19.43	10.79
HHV=25.235-0.328*ash-0.068*VM.....(20) (Jenkins and Ebeling, 1985)	Cassava peelings	84.17	7.99	7.10	15.59	16.89	8.34
	Plantain peelings	88.17	4.74	7.84	16.69	17.68	5.93
	Corn cob	92.50	0.75	6.75	21.78	18.70	14.14
HHV=10814.08+313.3*(VM+FC)...(21) (Jiménez and González, 1991)	Cassava peelings	84.17	7.99	7.10	15.59	17.78	14.05
	Plantain peelings	88.17	4.74	7.84	16.69	19.27	15.46
	Corn cob	92.50	0.75	6.75	21.78	20.28	6.89
HHV=0.312*FC+0.1534*VM.....(22) (Demirbas, 1997)	Cassava peelings	84.17	7.99	7.10	15.59	15.13	2.95
	Plantain peelings	88.17	4.74	7.84	16.69	15.97	4.31
	Corn cob	92.50	0.75	6.75	21.78	16.30	25.16
HHV=0.3536*FC+0.1559*VM-0.0078*ash (23) (Parikh <i>et al.</i> , 2005)	Cassava peelings	84.17	7.99	7.10	15.59	15.57	0.13
	Plantain peelings	88.17	4.74	7.84	16.69	16.48	1.26
	Corn cob	92.50	0.75	6.75	21.78	16.80	22.87
HHV=0.1905*VM+0.2521*FC.....(24) (Yin, 2011)	Cassava peelings	84.17	7.99	7.10	15.59	17.82	14.30
	Plantain peelings	88.17	4.74	7.84	16.69	18.77	12.46
	Corn cob	92.50	0.75	6.75	21.78	19.32	11.29

HHV: Higher heating value; AAE: Average absolute error

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

Models	Samples	C	H	N	O	Experimentals HHV value (MJ/kg)	Calculated HHV value (MJ/kg)	AAE (%)
HHV=-1.005+0.348*C-1.073*H+0.222*O.....(25) (Jenkins and Ebeling, 1985)	Cassava peelings	35.26	6.48	2.42	54.10	15.59	16.32	4.70
	Plantain peelings	44.38	6.12	0.83	46.76	16.69	18.25	9.37
	Corn cob	49.13	6.05	0.24	44.35	21.78	19.45	10.71
HHV=0.3699*C+1.3178... (26) (Demirbas and Demirbas, 2004)	Cassava peelings	35.26	6.48	2.42	54.10	15.59	13.94	4.46
	Plantain peelings	44.38	6.12	0.83	46.76	16.69	17.67	5.87
	Corn cob	49.13	6.05	0.24	44.35	21.78	19.61	9.96
HHV=3.55*C <sup>2</sup> -232*C-2230*H+51.2*C*H +131*N+20.600.... (27) (Friedl <i>et al.</i> , 2005)	Cassava peelings	35.26	6.48	2.42	54.10	15.59	14.40	7.64
	Plantain peelings	44.38	6.12	0.83	46.76	16.69	17.66	5.83
	Corn cob	49.13	6.05	0.24	44.35	21.78	19.53	10.33
HHV=0.3259*C+3.4597.... (28) (Sheng and Azevedo, 2005)	Cassava peelings	35.26	6.48	2.42	54.10	15.59	14.95	2.47
	Plantain peelings	44.38	6.12	0.83	46.76	16.69	17.92	7.37
	Corn cob	49.13	6.05	0.24	44.35	21.78	19.47	10.61

HHV: Higher heating value; AAE: Average absolute error

**Table 4:** Models based on the structural composition

Models	Samples	Cellulose	Hemicellulose	Lignin	Exp HHV value (MJ/kg)	Cac HHV value (MJ/kg)	AAE (%)
HHV = 0.0889L + 16.8218....(29) (Demirbas, 2001)	Cassava peelings	133.2	220.9	129.1	15.59	15.31	7.64
	Plantain peelings	127.3	110.9	18.3	16.69	18.20	14.67
	Corn cob	470.3	247.8	142.2	21.78	19.88	11.82
HHV = 0.0877L + 16.4951... (30) (Demirbas, 2001)	Cassava peelings	133.2	220.9	129.1	15.59	17.65	13.21
	Plantain peelings	127.3	110.9	18.3	16.69	17.95	7.55
	Corn cob	470.3	247.8	142.2	21.78	18.62	11.56

L: Lignin; C: Cellulose; AAE: Average absolute error

**Table 5:** Molecular formula

Samples	Molecular formula	Designation	$\Delta rH^\circ$ (kJ/mo)	HHV e (MJ/kg)	HHV ca (MJ/kg)	AAE (%)
Cassava peelings	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	Furfural	-19353.60	15.59	16.13	3.46
Plantain peelings	C <sub>5</sub> H <sub>8</sub> O <sub>4</sub>	Glutaric acid	-569.90	16.69	16.27	2.52
Corn cobs	C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>	Propenoic acid	-1441 <sup>c</sup>	21.78	20.02	8.08

AAE: Average absolute error

**Table 6:** Molecular model on twenty biomasses from literature

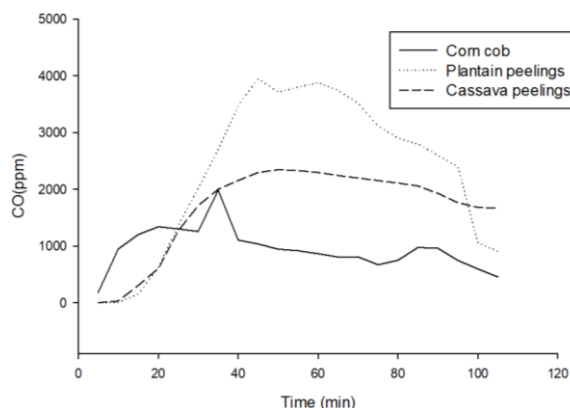
Samples	C (%)	H (%)	O (%)	Crude formula	Name	$\Delta fH^\circ$ (kJ/mol)	$\Delta rH^\circ$ (kJ/mol)	Exp HHV (Mj/kg)	Cal HHV (Mj/kg)	AAE %
Wood sawdust										
(Boumanchar <i>et al.</i> , 2019)	45.97	5.13	48.53	C <sub>3</sub> H <sub>2</sub> O <sub>2</sub>	2-Propynoic acid	-193.20	-13524.0000	18.21	18.18	0.160
Rice husk										
(Huang and Lo, 2020)	38.50	5.20	34.61	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	Furfural	-201.60	-19353.6000	14.69	16.13	9.800
Sugarcane bagasse										
(Huang and Lo, 2020)	45.48	5.96	45.21	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	Ethylene glycol	-460.00	-1182.0000	18.73	19.06	1.760
Cotton stalk										
(Munir <i>et al.</i> , 2009)	47.07	4.58	42.10	C <sub>5</sub> H <sub>6</sub> O <sub>4</sub>	Glutaric acid	-960.00	-569.9000	17.40	16.27	6.490
Corn stover										
(Duan <i>et al.</i> , 2018)	45.48	5.52	41.52	C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>	Acetic acid	-386.10	-970.9000	17.93	16.18	9.760
Coffee husk										
(Huang and Lo, 2020)	47.50	6.40	43.70	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	1,2 Propanedione	-309.10	-1441.0000	19.80	20.02	1.110
Sugar cane straw										
(Darvishan <i>et al.</i> , 2018)	43.50	6.10	41.10	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Acetic acid	-386.10	-970.9000	17.19	16.18	5.880
Forest residue										
(Nhuchhen and Afzal, 2017)	53.16	6.25	40.00	C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>	1,2 Propanedione	-309.10	-1441.0000	19.50	20.02	2.670
Rice straw										
(Boumanchar <i>et al.</i> , 2019)	38.24	5.20	36.26	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	Furfural	-201.60	-19353.6000	15.09	16.13	6.900
Corn straw										
(García <i>et al.</i> , 2013)	44.73	5.87	40.44	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	Glycerol	-669.60	-1650.2000	17.68	17.93	1.410
Banana leaves										
(De Oliveira <i>et al.</i> , 2014)	44.28	6.23	37.90	C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>	Acetic acid	-386.10	-970.9000	17.70	16.18	8.590
Corn cob										
(Boumanchar <i>et al.</i> , 2019)	44.78	6.02	48.77	C <sub>3</sub> H <sub>2</sub> O <sub>2</sub>	2-Propynoic acid	-193.20	-13524.0000	17.69	18.18	2.770
Coconut shell										
(Boumanchar <i>et al.</i> , 2019)	47.93	6.05	45.63	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	1,3,5-Trioxane	-522.50	-1513.0000	18.88	16.81	10.96
Coffee husk										
(Boumanchar <i>et al.</i> , 2019)	45.06	6.42	45.51	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Propanoic acid	-510.70	-1524.8000	19.33	20.60	6.570
Rice husk										
(Boumanchar <i>et al.</i> , 2019)	26.69	2.88	70.05	CHO	Oxomethyl	-43.10	-492.9000	15.90	16.99	6.860
Potato plant waste										
(Boumanchar <i>et al.</i> , 2019)	38.33	5.07	55.03	C <sub>3</sub> H <sub>4</sub> O <sub>3</sub>	Ethylene carbonate	-571.50	-1179.0000	14.07	13.40	4.760
Black poplar wood										
(Boumanchar <i>et al.</i> , 2019)	43.25	6.33	49.66	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Acetic acid	-386.10	-970.9000	18.17	16.18	10.95
Wheat straw										
(Boumanchar <i>et al.</i> , 2019)	45.58	6.04	46.60	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Acetic acid	-386.10	-970.9000	17.34	16.18	6.690
Walnut shell										
(Boumanchar <i>et al.</i> , 2019)	46.97	6.27	46.44	CH <sub>2</sub> O	Formaldehyde	-108.60	-569.9000	18.38	18.99	3.320
Briquette										
(Boumanchar <i>et al.</i> , 2019)	46.74	6.39	45.52	CH <sub>2</sub> O	Formaldehyde	-108.60	-569.9000	18.50	18.99	2.650

AAE: Average absolute error

**Table 7:** Volume of flue gas

Samples	Cassava peelings	Plantain peelings	Corn cob
V <sub>CO2</sub> (N m <sup>3</sup> /kg)	0.658 ±0.004 <sup>a</sup>	0.828±0.002 <sup>b</sup>	0.917±0.002 <sup>c</sup>
V <sub>H2O</sub> (N m <sup>3</sup> / kg)	0.762±0.018 <sup>a</sup>	0.686±0.014 <sup>b</sup>	0.678±0.004 <sup>b</sup>
V <sub>N2</sub> (N m <sup>3</sup> / kg)	0.019±0.002 <sup>a</sup>	0.007±0.001 <sup>b</sup>	0.002±0.001 <sup>c</sup>
V <sub>SO2</sub> (N m <sup>3</sup> / kg)	0.013±0.001 <sup>a</sup>	0.013±0.001 <sup>a</sup>	0.002±0.001 <sup>b</sup>
V <sub>O2</sub> (N m <sup>3</sup> / kg)	0.380±0.002 <sup>a</sup>	0.327±0.001 <sup>a</sup>	0.621±0.002 <sup>b</sup>
V <sub>a</sub> (N m <sup>3</sup> / kg)	4.022±0.062 <sup>a</sup>	4.082±0.024 <sup>a</sup>	3.033±0.029 <sup>b</sup>
V <sub>dSp</sub> (N m <sup>3</sup> / kg)	3.867±0.052 <sup>a</sup>	4.073±0.017 <sup>b</sup>	3.316±0.025 <sup>a</sup>
V <sub>wsp</sub> (N m <sup>3</sup> / kg)	5.021±0.073 <sup>a</sup>	4.875±0.029 <sup>b</sup>	4.934±0.026 <sup>ab</sup>
CO (ppm)	2345±23 <sup>b</sup>	4797±50 <sup>c</sup>	1983±20 <sup>a</sup>

V<sub>CO2</sub>: Volume of CO<sub>2</sub>; V<sub>H2O</sub>: Volume of H<sub>2</sub>O; V<sub>N2</sub>: Volume of N<sub>2</sub>; V<sub>SO2</sub>: Volume of SO<sub>2</sub>; V<sub>O2</sub>: Volume of O<sub>2</sub> V<sub>a</sub>: Combustion power V<sub>dSp</sub>: dry smoke power V<sub>wsp</sub>: wet smoke power. The numbers in the same line that have different letters are significantly different



**Fig. 1:** Evolution of CO production during combustion

Also coming from Table 1 that hemicellulose is higher in cassava peelings, while cellulose and lignin are closer. In plantain peelings, the value of cellulose and hemicellulose are closer and lignin reveals the lowest value. Cellulose is the highest in corn cob followed by hemicellulose and lignin. Cellulose is a polymer of glucose and its structure aid to have tightly packed polymer chains, resistant to depolymerization and highly crystalline structure (Rezania *et al.*, 2020; Xu and Hang, 2014). Hemicellulose is another carbohydrate component that has an amorphous, branched, and random structure that includes five or six carbon sugars (Rezania *et al.*, 2020). Lignin is an irregular polyphenolic biopolymer constructed of phenylpropanoid monomers with various degrees of methoxylation that are biosynthesized into a complex and highly heterogeneous aromatic macromolecule (Chico-Santamarta *et al.*, 2013). Furthermore, feedstock rich in cellulose and hemicellulose which are polymers of sugars can be considered a potential source to produce fermentable sugars (Rezania *et al.*, 2017). Cellulose and hemicellulose contents are also macromolecules used for biogas, bio-oil, and dried briquettes while lignin is recommended to be converted to coal. In the bioethanol process, cellulose and hemicellulose pass through acid or enzymatic hydrolysis to glucose, hexose, and pentose (Rezania *et al.*, 2017); while in the pyrolysis process, these biomolecules are transformed to bio-oil whereas in physical conversion cellulose can play binder role to form a well bond briquette. Lignin plays a very important role as a structural component that provides tensile strength and is converted into coal during the pyrolysis process. This coal can also be used to produce fuel briquettes (Samomssa *et al.*, 2022). Thus, cassava peelings can be used efficiently to produce bioethanol and biogas through the biochemical process, while corn cob can be used in the thermochemical or biochemical process and plantain peelings reveal an average efficiency in the thermochemical process.

From all these analyses, it can be concluded that the investigated biomasses can be efficiently used in biochemical conversion for bioethanol/biogas production,

in thermochemical conversion to produce bio-oil/syngas, and in the physical process to densify feedstock into briquette. The sulfur content of cassava and plantain peelings exceeded the 0.2% threshold (Table 1), meaning that corrosion and SO<sub>x</sub> emissions would probably be present during the thermal conversion process. The nitrogen content in cassava peelings is more than 0.6%, suggesting that NO<sub>x</sub> emissions could be expected (Virmond *et al.*, 2012). Hence, during gasification, the emission of NO<sub>2</sub> and SO<sub>2</sub> could be considered to limit corrosion.

#### *Verification of the Model Based on Ultimate Analysis, Proximate Analysis, and Structural Composition*

The modeling of the higher heating value as a function of proximate analysis is performed to establish a relationship between HHV and volatile matter, fixed carbon, and ash. Table 2 shows the experimental HHV and calculated HHV by applying the different models. The selected models are those based on experimental results on different biomasses. Due to the large number of models given in the literature, the selected models are those giving an average absolute error less than or equal to 25%. Six models were used. The equation of these models is presented in Table 2 (Jenkins and Ebeling, 1985; Jiménez and González, 1991; Demirbaş, 1997; Parikh *et al.*, 2005; Yin, 2011). All these models were constructed empirically by looking for a linear correlation between HHV and experimental data.

The average absolute error (%) with plantain peelings is less than or equal to 15%. The plantain peelings give the best correlation with these different models. The average absolute error of 1.26% with the model of Parikh *et al.* (2005) (Parikh *et al.*, 2005) indicates an excellent correlation. The correlation of the higher heating value of plantain peelings with the (Demirbaş, 1997) equation also gives a good correlation. Similarly, the experimental higher heating value of cassava peelings is well described by these two equations. It can be noted that the number of fibers in the cassava peelings and plantain peelings is two to three times lower than in the corn cobs (Table 1). This could explain the weak correlation between the higher heating value of corn cobs with its two equations. It can also be observed that the heating value of cassava peelings is less well correlated with the first three than that of the corn cob (Jenkins and Ebeling, 1985). The opposite effect is noted for the equations developed by Demirbas (1997) (Patrihk *et al.*, 2005; Yin, 2011). Approximate HHV models, based on the determination of proximate analysis, yield an average absolute error ranging from 1.3 to 25%, as derived from the experimental results.

Four models based on a linear or second-order polynomial relationship between the percentage of carbon, or the percentage of carbon, and the percentage of hydrogen were selected in the literature. The selected equations are presented in Table 3 (Jenkins and Ebeling,

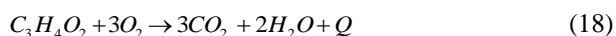
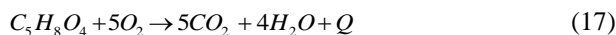
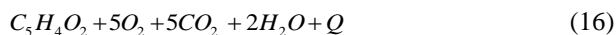
1985; Demirbaş and Demirbaş, 2004; Friedl *et al.*, 2005; Sheng and Azevedo, 2005). All the models taking into account the percentages of N and S gave low correlation (average absolute error greater than 25%) with the experimental results. All the average absolute errors are less than 15%, except for the correlation obtained with the (Yin, 2011) model for cassava peelings (Table 2). The models based on ultimate analysis gave better results than those based on the proximate analysis. The heating value of plantain peelings is better correlated with the five models than the higher heating values of other bioresources. The same result was observed by the models based on proximate analysis. The heating values of cassava peelings and corn cob vary greatly from one material to another and no consistent evolution appears to be apparent.

The average absolute error (%) of the models based on structural composition varies between 7.64 and 13.21% (Table 4). These values are less than 15%. The models based on structural composition give a good correlation compared to the models based on proximate analysis.

Investigation of the model based on proximate analysis, ultimate analysis, and structural analysis shows that the models based on ultimate analysis give the best correlation, followed by the model based on structural analysis. The elaboration of the models based on ultimate analysis takes into account many biofuels. This led to the use of the ultimate analysis to determine higher heating value by reducing the material to  $C_xH_yO_z$  compound and calculating its combustion enthalpy. Compared to other models, this one is not linear, because it uses molecular mass.

#### *Higher Heating Value from Combustion Enthalpy*

The molecular formula for cassava peelings is  $C_5H_4O_2$ , for plantain peelings is  $C_5H_8O_4$  and for corn cob is  $C_3H_4O_2$  (Table 5). It corresponds to furfural, glutaric acid, and propenoic acid, respectively. The corresponding combustion reactions are presented by the following equations:



The combustion enthalpy of the three bioresources is negative (Table 5) which makes them exothermic biomass. The average absolute error of higher heating values for the three investigated bioresources ranges between 2.52 and 8.08%. The low average absolute error was observed for plantain peelings, while the highest value was observed for corn cob. These average absolute errors are low compared to the average absolute error from the literature for the models based on proximate

analysis, ultimate analysis, and structural composition, which ranged from 4 to 10% (Parikh *et al.*, 2005; Soponpongpipat *et al.*, 2015). This hypothesis, although too simplistic, gives satisfactory results. It can be concluded that the higher heating value from combustion enthalpy takes into account only the ultimate analysis of bioresources without another hypothesis and augurs a better correlation. This way to calculate HHV was tested just on three bioresources. It may be judicious to test this model on other fuels from the literature.

#### *Higher Heating Value from Combustion Enthalpy Tested on Biomasses from Literature*

The higher average absolute error for the twenty investigated fuels is 10.96% and the lowest value is 0.16% (Table 6). This table also shows that amongst the investigated bioresources, four have residue of more than 7%. It is attributed to rice husk, coconut shell, corn stover, and banana leaves, whose residue is 9.80, 10.96, 9.76, and 8.59%, respectively. The reason could be the type of liaison between molecules. Oxygen content is the most important property of the fuels, which explains the combustion behavior. This value could justify the higher average absolute error. In the literature, the residues from the models based on proximate, ultimate, and structural analysis are between 4 and 10% (Parikh *et al.*, 2005; Soponpongpipat *et al.*, 2015). The residues obtained in this study are in this range.

It is important to mention that there is no relationship between the calculated higher heating values of the twenty investigated wastes. The calculated higher heating value depends only on the carbon, hydrogen, and oxygen of each lignocellulose waste. Compared to the linear models based on proximate analysis, ultimate analysis, and structural analysis, which consider many bioresources, this one is not linear and is very simplistic. The calculation of HHV from combustion enthalpy depends only on the carbon, hydrogen, and oxygen of the investigated bioresources. This way can be used for all types of fuel compared to the models based on proximate analysis, ultimate analysis, and structural analysis which are reliable only on a certain type of fuel. The table also shows that the combustion enthalpy of the twenty investigated bioresources is negative. This could justify the reason for using these bioresources for energy processes.

#### *Analyzing Flue Gases*

The knowledge of flue gas composition allows the prediction of combustion conditions and improves combustion efficiency. The components that are of interest from an environmental perspective are Nitrous Oxides (NO<sub>x</sub>), CARBON dioxide (CO<sub>2</sub>), Carbon monoxide (CO), and Sulfur Dioxide (SO<sub>2</sub>). The result is in agreement with the ultimate analysis previously presented with high content of C, H, and O (Table 1). The volumes of  $V_{CO_2}$ ,  $V_{H_2O}$ , and  $V_{O_2}$



are the highest for each material while  $V_{N_2}$  and  $V_{SO_2}$  are the lowest (Table 7). The volume of water gas is higher for cassava peelings, while for corn cobs and plantain peelings, the volume of carbon dioxide is higher. It is also apparent from Table 7 that the comburivorous power is lower for corn cobs and higher for plantain peelings. In the presence of excess oxygen, the sulfur dioxide which derives from any sulfur-containing compounds in the fuel is oxidized to sulfur trioxide ( $SO_3$ ) and at higher temperatures, approximately  $800^\circ C$ , the formation of sulfur trioxide is favored.  $SO_2$  combination with water or condensate, Sulphurous Acid ( $H_2SO_3$ ), and Sulphuric Acid ( $H_2SO_4$ ) are produced, both of which are linked to numerous types of environmental damage to vegetation and building fabrics.  $NO_2$  in particular is a dangerous respiratory poison and, in combination with sunlight, contributes to the destruction of ozone. In the practice of ventilated boilers, it is recommended to choose the fuel with the lowest comburivorous power because of the small quantity of air needed and also for the low greenhouse gas production. These values compared to gases are the lowest. This could explain the higher heating value of gases. Wet smoking power is higher than dry smoking power. This is because dry smoke power does not take water into account. The low dry smoke power of corn cobs justifies their low gas (CO) emissions into the atmosphere and the energy is not dissipated in the fumes. This result is in agreement with the CO emitted into the atmosphere which gives a low value for corn cobs. The oxygen present in the biomass is not enough to induce complete combustion and it is necessary to supply the secondary air in the combustion room.

#### Carbon Monoxide Behavior During Combustion

The quantity of carbon monoxide released during combustion looks the same for the three biomasses (Fig. 1). This quantity increases for the first 50 min and decreases starting from the 60<sup>th</sup> min. Plantain peelings show a higher value of CO and corn cobs and cassava peelings present a lower value of around 2000 ppm. These values are higher than that recommended by the European standard for household waste incineration which limits the metal discharge to less or equal to  $50 \text{ mg/Nm}^3$ . However, the amount of carbon monoxide released during combustion depends on the amount of oxygen. The high quantity of oxygen decreases the CO released. Thus, a supplementary supply of oxygen or combustion in the ventilated system can reduce the monoxide carbon amount. Compared to the literature the result of CO released varies from one article to another (Pilusa *et al.*, 2013; Gimbutaite and Venckus, 2008). This could justify by the quantity of oxygen which varies in function of experimental conditions.

#### Conclusion

The aim of this study was the investigation of efficient thermal conversion technologies and the exploration of the calculation of HHV from combustion enthalpy for the

prediction of HHV on the most abundant biomasses in Cameroon. The results show that cassava peelings, plantain peelings, and corn cobs can be efficiently used in thermochemical conversion to produce bio-oil and syngas and in the biochemical process to produce bioethanol and biogas. Flue gas reveals a value less than the toxic values fixed by the European standard for household waste incineration and can therefore be used as an environmentally friendly bioenergy source. The levels of S and N could be taken into account in the design of a gasification plant to control the emission of  $NO_2$  and  $SO_x$ -derived pollutants as their value is more than the limit fixed. HHV from combustion enthalpy gives the average absolute error of 2.52% for plantain peelings, 3.46% for cassava peelings, and 8.08% for corn cobs. This way to calculate HHV shows the best correlation compared to the models based on proximate analysis, ultimate analysis, and structural analysis, whose average absolute error ranged from 4 to 10%. Enthalpies of reaction of all investigated biomasses are negative and could justify their high energy content.

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#### Author’s Contributions

All authors equally contributed to this study.

#### Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and that no ethical issues are involved. In addition, the order of authors has been approved by all authors.

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## Highlights

- Ultimate, proximate and structural analysis of cassava peelings, plantain peelings and corn cobs from Cameroon
- Efficient thermal conversion technologies
- Comparison between model based on proximate analysis, ultimate analysis and structural analysis to predict higher heating value
- Reducing biomasses on molecular formula using ultimate analysis
- Elaboration of molecular model to predict heating value

## Nomenclature

<b>AAE:</b>	Average absolute error
<b>C:</b>	Carbon (%)
<b>H:</b>	Hydrogen (%)
<b>N:</b>	Nitrogen (%)
<b>S:</b>	Sulfur (%)
<b>O:</b>	Oxygen (%)
<b>MC:</b>	Moisture content (%)
<b>VM:</b>	volatile Matter (%)
<b>FC:</b>	Fixed Carbon (%)
<b>%:</b>	Percentage
<b>LHV:</b>	Low heating value (MJ/kg)
<b>HHV:</b>	High heating value (MJ/kg)
<b>MJ/Kg:</b>	Mega joule per kilogram
<b>L:</b>	Lignin;
<b>Ce:</b>	Cellulose;
<b>He:</b>	hemicellulose