Residual biomass from Brazil´s Pantanal and Cerrado – HHV and ultimate analysis estimations from experimental results for proximate analysis

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Abstract:

This paper presents results of experimental evaluation, and estimates of the energy characteristics for typical residual biomass in Brazil's midwest at Mato Grosso do Sul state, namely, Bocaiúva/Macaúba husk (*Acrocomia aculeata*), Crambe bran (*Crambe abyssinica*) and Corncobs. The methodology has support on ABNT technical standards and scientific literature, for specific mass, proximate analysis, ultimate analysis and determination of the HHV - Higher Heating/Calorific Value. Additionally, equations proposed in the literature for biomass analysis allows quickly and inexpensive estimations for ultimate analysis (elemental composition) and HHV taking into account proximate analysis values for the biomass samples. Appropriate instruments/equipments like melting pot, analytic balance, drying and sterilization kiln, desiccators and muffle furnace, were used to perform the measurement of quantities of interest. Results are analyzed and discussed for specific mass (kg/m³), moisture, volatile matter, ash, fixed carbon and organic matter contents (%), ultimate analysis (%), HHV (kJ/kg) to each of the residual biomass samples evaluated in this work. Preliminary experimental results indicated that Crambe bran's HHV is around 22 MJ/kg, while correlations in this work indicated ~18 MJ/kg for both Crambe bran and Corncobs and ~19 MJ/kg for Bocaiúva husks. Those values are higher than most common residual biomasses from agricultural crops in Brazil: rice husk (12.9 MJ/kg), soybean hulls (16.9 MJ/kg) and sugarcane bagasse (17.3 MJ/kg).

Keywords:

Biomass, Biofuels, Renewable energy, Combustion, Energetic characteristics.

1. Introduction

Biomass is one of the most important sources to increase the production of energy based on renewable energy sources and do not affect the overall balance of CO_2 in the atmosphere, as pointed on [1]. The conversion of green energy from biomass originated by agricultural and industrial energy processes is pursued by various research institutions around the globe. This concept is being considered for both systems that generate and consume large volumes of primary and final energy, and for independent power producers which commonly use biomass residues from their processes to meet their energy needs [2].

Brazil is considered one of the largest agricultural producers due to its large area available and biodiversity and therefore is a strong supplier of agricultural waste, i.e., residual biomass. These biomass residues can be transformed by means of physical, chemical and biological processes, but for this to occur properly, these solid fuels should be characterized for their properties are known. This characterization can be based on the physical characteristics (particle size, density/specific mass and moisture content), by proximate analysis (moisture, volatile, ash and fixed carbon) and ultimate analysis (which analyzes the chemical elements present in biomass), summative analysis and heat power [3].

The heating value of biomass is an indication of the energy released in combustion processes and is provided by the heat produced in the breaking of bonds between molecules that form. The literature [4] indicates that the creation and control of a biomass combustion chamber strongly depend on the calorific value of the biomass fuel.

Numerous equations have been published in the literature, as in [4] *apud* [5], to estimate the fuel heating value from ultimate analysis (elemental composition) or from proximate analysis (mass fractions for: volatile matter, ash and fixed carbon). The higher heating value (HHV) is given for standard conditions (101.3 kPa, 25°C) of all products and includes the condensation enthalpy of water. The net or low heating value (LHV) is obtained when the condensation enthalpy of water is not included [1]. These correlations from the literature provide a quick answer to energy order of magnitude.

Authors of the present work are conducting experiments with typical biomasses from Brazil´s Pantanal and Cerrado, crops and natural species. Thus, for quick estimations of HHV and elemental compositions, correlations from literature were considered. Methodology is being improved in recent works, as in [6], in order to understand its characteristics and propose ways to quantify energy values available for regional applications as solid fuels.

2. Methodology

Biomass experimental analyses were conducted at UFGD Energy Engineering facilities (Renewable Energy Laboratory). The reduction of the particle size of the Bocaiúva husk and Crambe bran were performed by using a Wiley mill SOLAB Sl3 (figure 1a). Drying of samples used a stove Sppencer scientific 420-1d (figure 1b). For the ash and volatile material analysis, it was used a muffle furnace Novus N1100 (figure 1c). For weighing the sample in all cases one Mark S3102- Precision Balance 3100g (0.01 g) of Bell Engineering (figure 1d) was used. To obtain the Crambe bran without oil, separation was performed by using an oil extractor ECIRTEC MPE-40PI (figure 1e).

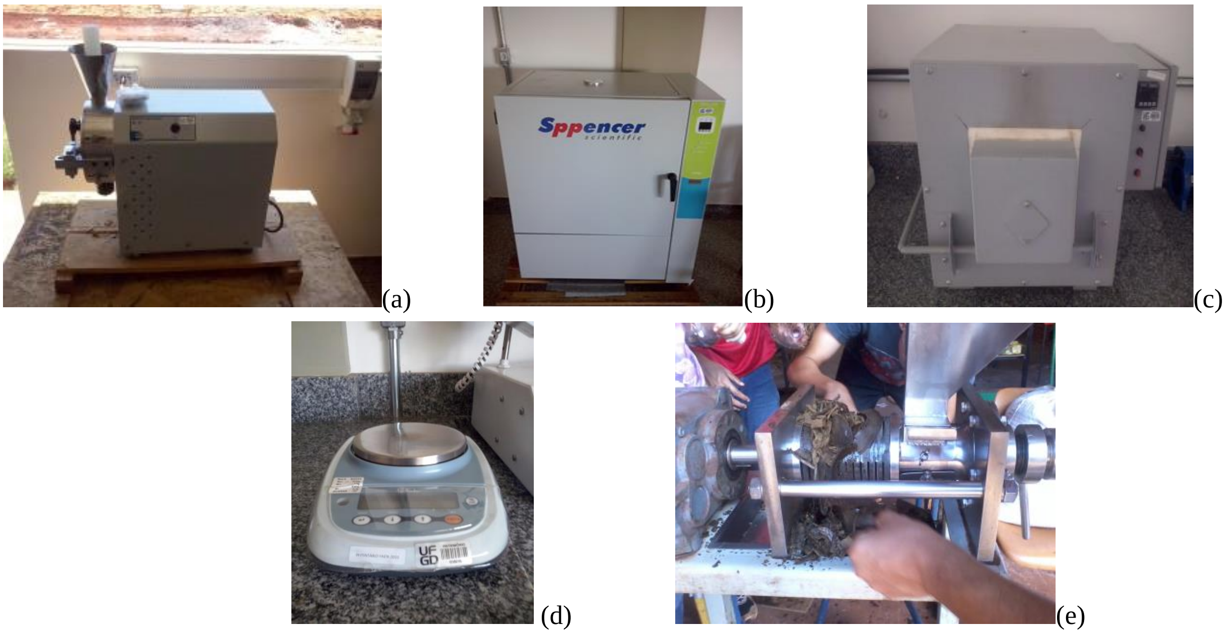

Fig. 1. Equipments at energy engineering facilities (UFGD, Dourados-MS, Brazil).

2.1. Biomass samples – obtaining and preparation

Biomass is mainly composed by cellulose $(C_6H_{10}O_5)_n$, hemicelluloses and lignin. It is usually defined as any organic matter mainly containing carbon (C), hydrogen (H), oxygen (O) and nitrogen (N). The following residual biomass samples were obtained and prepared for analysis: Crambe bran (figure 2a), Bocaiúva husk (figure 2b) and Corncobs (figure 2c). First sample was obtained at EMBRAPA CPAO, second one at UFGD Food Engineering laboratories and third one from UFGD farming field. All samples were milled (figure 1a) previously to proximate analysis procedures.

Crambe (*Crambe abyssinica*) is an oleaginous plant belonging to the family of Cruciferae which oil can be used as raw material for biodiesel production. In the oil extracting process, large amounts of residues (Crambe bran) occurs, 56.8-67.6% of the original biomass. Bocaiúva (*Acrocomia aculeata*) is a native fruit to Brazil´s Central West, which pulp and nuts are used as food, but the Bocaiúva's chestnut has a very large percentage of oil that can be used to biodiesel production, as pointed out in recent works [7]. Corncobs are usually residual biomass from corn fields harvesting.


(a) (b) (c)

Fig. 2. Biomasses from Brazil´s pantanal and cerrado environment.

2.2. Proximate analysis

Biomass proximate analysis was considered in accordance to NBR 8112, [8]. That standard is for charcoal that is also a solid biofuel whose raw material is typically wood from threes subjected to thermal conversion via pyrolysis. It determines the mass fractions for contents of: moisture, volatile matter, fixed carbon and ashes. The moisture content shows the amount of water present in the sample at ambient temperature and pressure, it can be expressed on a wet (*wb*) or dry basis (*db*). The volatile matter content expresses the mass of the sample which volatilizes during heating. The ash content refers to the mass of the sample does not undergo combustion [9].

2.2.1. Moisture content (MC)

Take the melting pot to the stove at 105±5°C for a certain time for each biomass sample and register its mass after drying. Drying times was previously evaluated by ARENA research group in other works as [6], and reference drying times for Bocaiúva husk, Crambe bran and Corncobs were respectively: 30 minutes, 40 minutes and 60 minutes. Take 1g of biomass sample in each pot and leave it in the stove for the time previously determined for complete drying. Register total mass before and after biomass drying by using a precision balance. Calculate the moisture content by Eqs. (1) and (2):

$$MC_{wb}(\%) = \left(m_{H2O} / m_{BS,in-natura}\right).100 \qquad (1)$$

$$MC_{db}(\%) = \left(m_{H2O} / m_{BS,dried}\right).100 \qquad (2)$$

Where MC_{wb} and MC_{db} are the Moisture Content (%) in wet (*wb*) or dry basis (*db*), respectively. m_{H2O} is the water mass (kg), $m\_{BS,in-natura}$ (kg) is the mass of *in natura* biomass and $m\_{BS,dried}$ (kg) is the mass of the biomass after drying.

2.2.2. Ash Content (AC)

Take the melting pot to the muffle furnace at 700±10°C for 20 minutes to have it completely dried. Measure the mass of dried melting pot before and after adding the dry biomass in it. Bring the melting pot to the muffle furnace at 700±10°C. As for the analysis of the ash content, the samples of Bocaiuva husk, Crambe bran and Corncobs stabilized after, respectively: 40 minutes, 60 minutes and 100 minutes. Thus, authors considered 100 minutes in the muffle furnace as standard time (when AC analysis) for all three biomass samples in this work. At the end, remove the melting pot from the muffle furnace, wait it to cool down and register the measured masses. Calculate the AC by Eq. (3):

$$AC(\%) = \left(m_{ash} / m_{BS,dried}\right).100 \tag{3}$$

Where AC represents the ash content (%), M_{ash} represent mass of ashes (kg) and $M_{BS,dried}$ represent the mass of dried biomass (kg).

2.2.3. Volatile matter content (VM)

Take the melting pot with cover to the muffle furnace at 900± 10°C for 10 minutes, according to ABNT standards [8]. Measure and register the mass of the melting pot with cover, after drying. Add dry biomass to each melting pot. Put it at door of the muffle furnace at 900±10°C for 3 minutes and then leave it inside for another 7 minutes. Remove the melting pot, let it cool down and register the measure masses. Determine the volatile matter content by Eq. (4):

$$VM(\%) = \left(m_{VM} / m_{BS,dried}\right).100 \tag{4}$$

VM (%) represent the content of volatile material and m_{VM} (kg) is the mass of volatile material.

2.2.4. Fixed carbon content (FC) and organic matter content (OM)

$$FC(\%) = 100 - (AC + VM) \tag{5}$$

$$OM(\%) = 100 - (AC) \tag{6}$$

2.3. Estimations for ultimate analysis and HHV

Biomass ultimate analysis (elemental composition) and HHV determination via experimental procedures usually consider as reference NBR-8112 and NBR-8633, [8] and [10]. Ultimate analysis determines the mass fraction for carbon (C), hydrogen (H), nitrogen (N2), sulfur (S), ashes (A) and other elements, if they exist. As high the C/H relationship in relation to the C/O relationship, higher is the energy contained in the biomass (HHV, J/kg) [11].

According to [9] there are two kinds of heating values: HHV which represents the maximum amount of thermal energy that can be obtained by heat releasing from the material undergoing combustion; LHV (lower heating value) which represents the same amount of HHV minus the amount of thermal energy necessary to return the superheated water content from vapor state into liquid state.

However, for a quick and low cost determination, it is possible to use mathematical correlations available in the technical-scientific literature as the ones pointed out in next equations.

- Ultimate Analysis [12] – Correlations for H, O and C

$$H(\%) = 0.052(FC) + 0.062(VM) \tag{7}$$

$$O(\%) = 0.304(FC) + 0.476(VM) \tag{8}$$

$$C(\%) = -0.637(FC) + 0.0455(VM) \tag{9}$$

Where FC is the Fixed Carbon mass fraction (%) and VM is the Volatile Matter mass fraction (%).

- Heating Values [4] and [13] – Correlations for HHV and LHV

✓ LHV in function of proximate analysis:

$$LHV = -116 - 1.33(AC) - 0.005(VM) + 1.92(VM + AC) - 0.0227(VM + AC) - 0.0122(VM)^2 + 6133(OM)^{-1} - 0.82(AC) \tag{10}$$

$$LHV = +46.6 - 1.19(VM + AC) + 0.00409(VM)^2 + 0.0179(AC)^2 - 0.0118(FC)^2 + 4634(OM)^{-1} + 0.23(AC)^{-1} \tag{11}$$

$$LHV = -5.9 + 0.836(FC) + 0.0116(FC)^2 + 0.00209(VM)^2 + 0.0325(AC)^2 \tag{12}$$

✓ HHV as function of LHV:

$$HHV = LHV + 2440[9(H) + MC] \tag{13}$$

✓ HHV as function of proximate analysis:

$$HHV = 0.353(FC) + 0.1559(VM) - 0.0078(AC) \tag{14}$$

$$HHV = 19914 - 0.2324(AC) \tag{15}$$

$$HHV = -3.0368 + 0.2218(VM) + 0.2601(FC) \tag{16}$$

$$HHV = 0.3536(FC) + 0.1559(VM) - 0.0078(AC) \tag{17}$$

✓ HHV as function of ultimate analysis:

$$HHV = 0.3259(C) + 3.4597 \tag{18}$$

$$HHV = 0.43738(C) - 1.6701 \tag{19}$$

2.4. Specific mass determination (ρ)

Biomasses specific mass, ρ (kg/m^3) and its uncertainty due to specific mass determination, $u(\rho)$, were calculated by Eqs. (20) and (21). Samples preparation was as indicated in item 2.1 of this work.

$$\rho\left(kg/m^3\right) = m_{sample}/V_{sample} \tag{20}$$

$$u_\rho = \sqrt{\left(\frac{\partial\rho}{\partial m}\right)^2 + \left(\frac{\partial\rho}{\partial V}\right)^2} = \sqrt{\left(u_m \cdot \frac{1}{V_{sample}}\right)^2 + \left(u_V \cdot \frac{-m_{sample}}{V_{sample}^2}\right)^2} \tag{21}$$

$u(\rho)$: Uncertainty due to specific mass determination.

As can be observed, V_{sample} contributes in two terms in Eq. (21) for the uncertainty while m_{sample} contributes in a single term but is more significant. Uncertainties from measurement instruments are: u_m = ±0.01 g, u_V = ±1 ml.

3. Results and discussion

In Table 1, we have the experimental results and its respective uncertainty, for proximate analysis of three biomass samples from Brazil's Pantanal and Cerrado. Around 10 samples of each selected biomass were considered in the analysis of the present work. As can be noticed, MC_{wb} and MC_{db} are close values, typically lower than 1% differences, and that is the characteristics of these biomasses from Pantanal environmental (Bocaiúva husk) and Cerrado crops (Crambe bran). MC_{wb} and MC_{db} are even lower for corncobs results which are *in natura* dry matter similar to dry straw.

Table 1. Proximate analysis results (%).

	MC_{wb} (%)	MC_{db} (%)	AC (%)	VM (%)	FC (%)	OM (%)
Bocaiúva husk	7.99 ±0.60	7.40 ±0.52	3.51 ±0.73	74,92 ±1.19	21.36 ±1.51	96.46 ±0.68
Corncobs	7.38 ±1.88	7.00 ±1.90	2.00 ±1.41	88.87 ±1.50	8.13 ±1.49	96.75 ±0.50
Crambe bran	8.70 ±0.79	8.00 ±0.67	7.14 ±1.21	76.74 ±1.05	15.68 ±2.14	92.43 ±1.95

Table 2 presents the results for ultimate analysis (elemental composition), based on Eqs. (7), (8) and (9). Results in Table 3 are obtained by applying correlations for LHV, i.e., Eqs. (10), (11) and (12). LHV values obtained have a negligible difference between them. Results in Table 2 and 3 are function of the parameters in Table 1.

Table 2. Ultimate analysis (%) from literature correlations.

	H (Eq. 7)	O (Eq. 8)	C (Eq. 9)
Bocaiúva husk	5.6	41.4	46.7
Corncobs	5.9	44.8	45.6
Crambe bran	5.6	41.3	44.9

Results in Table 2 indicate a relationship of O/C ~0.88 (41.4/46.7) and H/C ~0.12 (5.6/46.7), for the Bocaiúva husk, and O/C ~0.92 (41.3/44.9) and H/C ~0.13 (5.9/44.9) for the Crambe bran, and O/C ~0.98 (44.8/45.6) and H/C ~0.13 (5.9/45.6) for the Corncobs. According to [11] that mean that Bocaiúva husk should have the higher HHV, and Corncobs should have the lower.

Table 3. Heating values (MJ/kg) from literature correlations, LHV = f(proximate analysis).

	LHV f (Eq. 10)	LHV F (Eq. 11)	LHV f (Eq. 12)
Bocaiúva husk	18.8	19.0	18.8
Corncobs	18.1	17.9	16.8
Crambe bran	18.6	18.8	18.3

Table 4 has 3 HHV results obtained from the same equation (Eq. 13), as one of the parameters of the equation is the LHV which had its estimated using equations 10, 11 and 12 (Table 3).

Table 4. Heating values (MJ/kg) from literature correlations, HHV = f(LHV)

	HHV (Eq. 13) from Eq. (10)	HHV (Eq. 13) from Eq. (11)	HHV (Eq. 13) from Eq. (12)
Bocaiúva husk	20.2	20.4	20.2
Corncobs	19.5	19.3	18.2
Crambe bran	20.1	20.3	19.7

Figure 3 shows the behaviour of HHV and LHV for three biomass samples analyzed. It is noticeable that they present a linear behaviour, once the correlations considered were based on mathematical models from the literature.

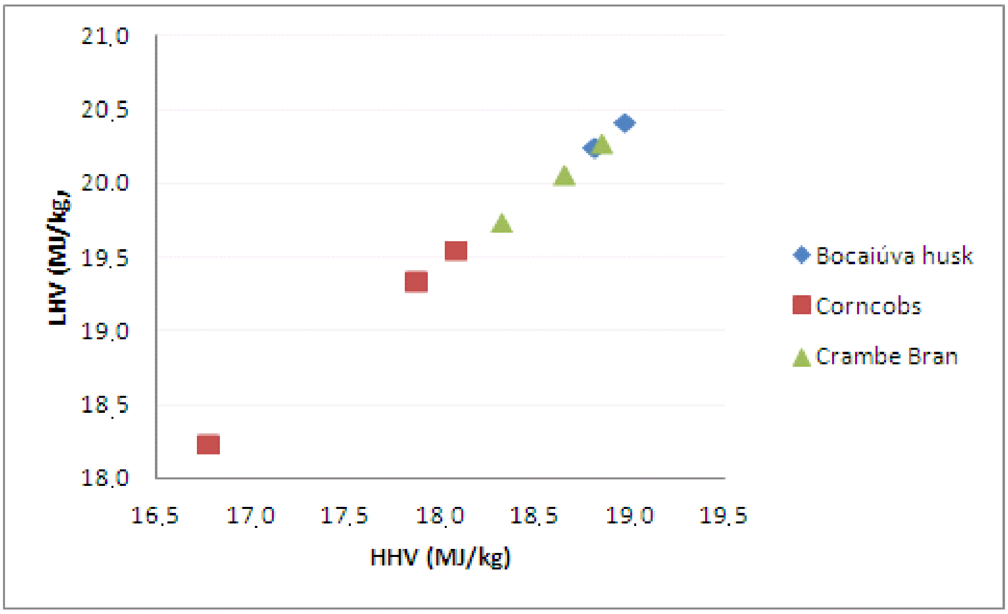

Fig. 3. HHV versus LHV for three residual biomasses from Brazil´s Pantanal and Cerrado.

Table 5 show the results of the HHV obtained of equations (Eq. 14 - 17), which parameters are proximate analysis. And Table 6 has the results of the HHV correlations with equations (Eq. 18 and Eq. 19) that use ultimate analisys as parameters. As we can observe in both tables, HHV for Bocaiúva husks are quite consistents and mean values are ~19.1 MJ/kg and ~18.8 MJ/kg, followed by Crambe bran with HHV mean values of ~17.9 MJ/kg and ~18.3 MJ/kg, and finally Corncobs with mean values of ~17.8 MJ/kg and ~18.0 MJ/kg.

Table 5. Heating values (MJ/kg) from literature correlations, HHV = f(proximate analysis).

	HHV from Eq.(14)	HHV from Eq.(15)	HHV from Eq.(16)	HHV from Eq.(17)
Bocaiúva husk	19.2	19.1	19.1	19.2
Corncobs	16.7	19.4	18.8	16.7
Crambe bran	17.4	18.2	18.1	17.4

Table 6. Heating values (MJ/kg) from literature correlations, HHV = f(ultimate analysis).

	HHV from Eq. (18)	HHV from Eq. (19)
Bocaiúva husk	18.7	18.8
Corncobs	18.3	18.3
Crambe bran	18.1	18.0

Table 7 shows the results obtained for the specific mass (Eq. 20) of the biomass and its uncertainties (Eq. 21). Crambe bran is the most concentrated mass for the same amount of volume, followed by Bocaiúva husk and Corncobs.

Table 7. Specific mass (kg/m³) from experimental determination.

	Specific mass
Bocaiúva husk	631.8 ±47.3
Corncobs	268.2 ±41.4
Crambe bran	647.4 ±47.7

4. Final conclusions

Having the values of proximate analysis for the selected biomass, obtained experimentally, it was possible to estimate the ultimate analysis (elemental composition) of biomasses samples from the equations referenced in this work. By knowing the biomass results for proximate analysis and ultimate analysis (elemental composition), it was possible to estimate the biomass energy content (MJ/kg) from equations for high heating value (HHV) and lower heating value (LHV).

Therefore, this method is an alternative to get a first approach to the ultimate analysis, and heating values of residual biomass samples without the need for expensive and/or inaccessible equipment. Work in progress is to obtain and compare experimental HHV and the results obtained herein, as well as experimental results for thermo-gravimetric behaviors under a variety of conditions.

Residual biomasses from Crambe bran and Bocaiúva husk are the strong candidates to be used as solid fuels, due to its good combination of HHV and specific mass values. HHV from correlations seems to underestimate real experimental values, once a first result obtained in the labs indicated ~22 MJ/kg for the Crambe bran when compared to ~18 MJ/kg in this work, a difference of ~20%. Also, HHV obtained in this work are quite interesting, when compared to typical agricultural crops: rice husk (12.9 MJ/kg), soybean hulls (16.9 MJ/kg) and sugarcane bagasse (17.3 MJ/kg).

Also are going to be considered for future analysis, torrefaction processes in order to intensify its HHV, as well as peletization or briqueting in order to intensify its specific mass.

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