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*Research article***Evaluation of the bioenergy potential of agricultural and agroindustrial waste generated in southeastern Mexico****Nathaly A. Díaz Molina<sup>1</sup>, José A. Sosa Olivier<sup>1,\*</sup>, José R. Laines Canepa<sup>1</sup>, Rudy Solis Silvan<sup>2</sup> and Donato A. Figueiras Jaramillo<sup>3</sup>**<sup>1</sup> Pilot Plant 3 solid waste and atmospheric treatment, Academic Division of Biological Sciences, Juarez Autonomous University of Tabasco, Mexico<sup>2</sup> Comalcalco Higher Technological Institute, Comalcalco, Tabasco, Mexico<sup>3</sup> Coprocessing Laboratory, Geocycle® SA. of CV. Macuspana, Mexico**\* Correspondence:** Email: aurelio.sosa@ujat.mx, ing-jaso@hotmail.es; Tel: (+52) 9931940812.

**Abstract:** The generation of large volumes of agricultural and agroindustrial waste in the state of Tabasco represents a significant waste management challenge. We aimed to determine the bioenergy potential of five types of biomasses: Banana rachis, coconut shell, cocoa pod husk, sugarcane bagasse, and palm kernel shell, generated in agricultural and agroindustrial processes. This research involved characterizing and evaluating the energy quality of these biomasses by determining their calorific values and assessing their viability as fuel alternative sources. Additionally, we explored these biomasses' calorific value potential to reduce the inadequate disposal of wastes, reduce environmental impact, and provide alternative uses for these materials, which are typically discarded or have limited added value in the southeast region. The yield of waste generation per amount of production was estimated, with cocoa pod husk biomass and sugarcane bagasse, banana rachis, coconut shell, and palm kernel shell generating 0.685, 0.283, 0.16, 0.135, and 0.0595 kg of biomass per kg of crop, respectively. The bioenergy potential was evaluated through direct measurements using a calorimeter bomb, and indirect measurements using stoichiometric calculations. Four stoichiometric methods based on predictive equations were employed to determine the energy content of the biomasses from their elemental composition (Dulong, Friedl, Channiwala, Boie). The biomasses with the highest calorific values were coconut shell and cocoa pod husk, with values of  $16.47 \pm 0.24$  and  $16.02 \pm 1.54$  MJ/kg, respectively. Moreover, banana rachis had the lowest calorific value at  $13.68 \pm 3.22$  MJ/kg. The calorific values of the sugarcane bagasse and palm kernel shell were  $13.91 \pm 0.98$  and  $15.29 \pm 1.02$ , respectively. The factorial experimental design and statistical analysis revealed trends and magnitudes in the evaluation of energy determination methods and types of waste. The predictive equation of Dulong showed the highest similarity to the experimental values, especially for coconut shell ( $16.02 \pm 0.08$  MJ/kg). The metal content in biomasses such as palm kernel shell and coconut shell were below the limits established in ISO 17225:2014. Finally, our results indicated that coconut shell has superior characteristics for potential use as an alternative fuel, whereas banana rachis requires exploring alternative utilization options.

**Keywords:** biomass; calorific value; alternative fuels; waste management; elemental content

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## 1. Introduction

Waste generation is an inherent consequence of agricultural and agroindustrial production. The agricultural process involves crop production in agricultural, rural, and technified fields. The transition from agricultural to agroindustrial processes occurs by converting crop harvests into high value-added products in industrial facilities, which are subsequently incorporated into various distribution and consumption chains.

In 2021, the global agricultural land area was 4,787 million hectares (Mha), equivalent to 36.8% of the total land area [1]. By 2022, primary crop production reached 9.6 billion tons [2], valued at US\$3.47 trillion [3], contributing 4.3% to the Gross Domestic Product (GDP) of the global primary sector, which includes agricultural activities [4]. In Mexico, agricultural production reached 708.3 million tons on 20 million hectares in 2022 [5], with a value of US\$61.9 billion [3]. During the same period, primary activities contributed 4.1% to Mexico's GDP [4], and in the third quarter of 2023, an annual increase of 5.7% was recorded in these activities [6]. In the state of Tabasco, agricultural activity contributed 1.79% to the state GDP in 2021 [7]. In 2022, Tabasco produced 3.8 million tons on 256 thousand hectares, valued at US\$412.7 million [5], representing 0.54% of national agricultural production and placing the state in twenty-fourth place nationally. By the third quarter of 2023, the state primary sector saw an annual increase of 2% [8].

The use of renewable energy sources, such as wind, solar, hydroelectric, and biomass energy, allows for the consolidation of the sustainable development of human activities by combining or supplementing conventional resources to produce electrical or heat energy, helping to reduce the environmental impact. Many countries are developing studies that seek to enhance the use of biomass resources through processes such as anaerobic digestion, gasification, or combustion. Chauhan et al. [9] reports the potential waste generated by 12 crops in India. They consider the potential evaluation of biomass, considering the production, yield, and cultivated area of each crop; another guideline is the evaluation of the energy potential, and the application of some mathematical models; finally, the evaluation of gasification systems, where it would be possible to take advantage of biomass to transform it into electricity. In Mexico, Tauro et al. [10] report a study of the energy potential in producing pellets from agricultural and forestry residues, including sugarcane bagasse. The reported sugarcane pellets have a potential of 77 PJ/year, at a maximum production cost of 10.1 USD/GJ. Finally, the potential for mitigating GHG emissions in electricity production by replacing conventional fuel with biomass is estimated at 18%, which means a favorable environmental impact.

In Tabasco, the major crops in the agricultural sector are cocoa, coconut, banana, oil palm, and sugarcane, representing around of 80% of the state's production and around 50% of the cultivated area [5]. Specifically, sugar cane and oil palm crops are the most developed at the agroindustrial level. Although, the focus of agricultural production is on the tons produced and their economic value, the generated by-products often exceed the amount of primary production. For example, in cocoa production, only 10 to 20% of the fruit is utilized (beans or seeds), while 80 to 90% is discarded as waste (husks, mucilage or pulp, and shells) [11–14]. This high percentage of waste implies that for every ton of dry cocoa beans produced, 10 tons of cocoa pod husks are generated [15]. Similarly, one ton of banana production generates 4.08 tons of waste, with the pseudostem, leaves, skins, and rachis representing 73.53, 11.76, 10.78, and 3.92% of the total weight, respectively [16]. In coconut

cultivation, each tree produces approximately 70 to 150 fruits annually [17], with the shell (endocarp) representing 12 to 15% of fruits' weight [17–19]. In sugarcane production, for every ton of sugarcane milled, approximately 114 kg of sugar [20] and 150 to 286 kg of residual bagasse are generated [20–22]. In palm oil production, processing one ton of fresh fruit generates 23% empty fruit bunches, 15% mesocarp fibers, and 6% palm kernel shells [23,24]. Some of these biomass by-products are typically used under certain conditions as primary fuel, crop field amendments, raw material for value-added products, and animal feed.

Given the economic, social, and cultural importance of these crops, the management of their waste should be equally prioritized (Table 1). Cocoa pod husks are generated during the breaking process to obtain cocoa beans [25] and disposed of at the breaking or harvesting site [13,26]. During banana fruit harvesting, the rachis is discarded in the harvesting area and decomposes naturally without further use [16,27]. Green coconut production generates significant waste, including skin, husk, and shell, primarily due to coconut water extraction [28]. After copra extraction for oil production and other agroindustrial products [29], the coconut shell (endocarp) is often eliminated through open burning [30], with or without energy recovery. Bagasse, a fibrous waste from the sugarcane juice extraction process in the sugar industry [21,31], is used as an alternative fuel in boilers for heat, steam, and electricity co-generation [32]. Palm kernel shell waste, generated prior to palm oil extraction, is often used as an alternative fuel, or burned without energy recovery [33]. The inadequate final disposal of the waste generated causes alterations in the physical and chemical properties of the soil, high CO<sub>2</sub> emissions due to uncontrolled burning, as well as contamination of bodies of water, generation of unpleasant odors, and proliferation of rodents and insects and, therefore, the appearance of health problems in humans and animals.

**Table 1.** Main agricultural wastes and their respective crops [34].

Waste	Crop	Author	Waste	Crop	Author	Waste	Crop	Author
Bagasse	Agave	[35]	Straw	Barley	[36]	Leaves	Banana	[16]
	Malt	[37]		Wheat	[38]		Bamboo	[39]
	Sugarcane	[40]		Rice	[40]		Maize	[41]
	Sorghum	[42]		Oats	[36]		Tomato	[40]
	Cassava	[40]		Maize	[43]		Sugarcane	[44]
Bran	Wheat	[38]	Stubble	Maize	[40]	Pulp	Coffee	[45]
	Barley	[46]		Pineapple	[40]		Apple	[47]
Husk	Barley	[48]	Stalks	Grapes	[49]	Shells	Coconut	[50]
	Cocoa	[13]		Wheat	[41]		Jatropha	[51]
	Rice	[40]		Potato	[40]		Walnut	[38]
	Coffee	[40]		Tobacco	[52]		Peanuts	[53]
	Coconut	[54]		Cassava	[40]		Oil palm	[55]
Fiber	Oil palm	[55]	Pseudostem	Banana	[16]	Rachis	Banana	[16]
Peel	Banana	[16]	Stems	Bamboo	[56]	Seeds	Tomato	[40]
	Potato	[40]		Tomato	[57]		Orange	[40]
	Orange	[40]		Cassava	[58]		Grapes	[59]
	Pineapple	[40]		Cotton	[60]		Olive	[61]
	Oil palm	[62]		Soybean	[63]		Sugarcane	[64]
Fronds	Oil palm	[62]	Hulls	Soybean	[63]	Vinasse	Sugarcane	[64]
Crown	Pineapple	[40]	Cobs	Maize	[48]	Empty fruit bunch	Oil palm	[55]

Biomass from agricultural and agroindustrial crops can provide value-added products such as biofuels, contributing significantly to sustainable development and environmental conservation efforts. Biofuels can be solid (biochar), gaseous (biogas), and liquid like bio-oil, biodiesel, and bioethanol [65]. Researchers have demonstrated the adsorption capacity of biochar and activated carbon obtained from

precursor materials such as corn cob, sugarcane bagasse, and coffee husk for dye removal [66,67] and toxic metals like cadmium, mercury, and lead [68]. The potential of cocoa pod husk biochar as an alternative fertilizer to conventional chemical fertilizers (NPK) has also been evaluated [69,70]. Biogas has been obtained through the anaerobic digestion of sugarcane bagasse and peanut shells [71,72]. Bio-oils can be extracted from crops such as rice straw, cotton stalk, palm kernel shell, coconut shell, and sugarcane bagasse [29,55,73,74]. Biodiesel can be produced from palm kernel shells [75], while bioethanol is obtained from sources like banana rachis, sorghum, maize, wheat, barley, and sugarcane bagasse [75,76]. Biomass can also be used in concrete manufacturing using coconut shells [77,78] and leachate from banana rachis can be employed in crop fertilization [79]. The efficiency of biomass-to-power conversion depends on the characteristics of the biomass feedstock, particularly its calorific value or High Heating Value (HHV) [17]. HHV is typically determined experimentally using an adiabatic bomb calorimeter, a method that, despite being expensive, time-consuming, and error-prone [80], is widely replicated and commonly used for monitoring energy capacity in biomasses. Therefore, mathematical correlations based on proximate and ultimate analysis have been developed to predict the heating value of biomass. Table 2 presents a compilation of proximate and ultimate analysis data, as well as experimentally determined calorific values, for various biomass samples from published sources.

In Table 2, the HHV of banana rachis, cocoa pod husk, coconut shell, palm kernel shell, and sugarcane bagasse ranges between 13.479–16.96 MJ/kg, 12.48–18.87 MJ/kg, 17.35–20.498 MJ/kg, 12.24–20.35 MJ/kg, and 14.4–18.73 MJ/kg, respectively. It should be noted that, according to the different authors mentioned in Table 2, CCo has the highest calorific value and PPI has the lowest calorific value of the five biomasses analyzed.

**Table 2.** Summary of biomass wastes characteristics.

Biomass	Proximate analysis (%)				Ultimate analysis (%)					Lignocellulosic composition (%)			HHV (MJ/kg)	Author's
	Moisture	Ash	Volatile matter	Fixed carbon	C	H	O	N	S	Cellulose	Hemicellulose	Lignin		
Banana	-	28.50	-	-	-	-	-	-	-	35.30	17.90	76.5	-	[81]
rachis	5.1	24.7	58.4	11.6	32.5	4.6	36.4	1.6	-	-	-	-	13.48*	[82]
	-	25.85	-	-	-	-	-	-	-	33.5	7.8	15.6	-	[83]
	-	7.90	73.32	18.78	42.40	-	-	0.94	-	-	-	19.2	16.96	[84]
	19	-	-	-	-	-	-	-	-	42	13	12	-	[85]
	-	26.6	-	-	-	-	-	-	-	26.4	10.2	9.4	-	[86]
Cocoa	-	4.41	75.03	20.56	43	5.69	44.38	2.10	0.41	-	-	-	17.85	[87]
pod	10.29	10.81	68.47	10.43	43.87	5.82	47.28	2.23	0.57	30.41	11.97	33.96	17.93	[88]
husk	3.8	11.38	67.13	21.49	43.55	5.18	38.51	1.39	-	-	-	-	16.49	[89]
	14.43	6.99	58.75	19.83	48.82	7.89	39.85	1.95	1.49	-	-	-	18.87	[90]
	10.5	8.8	59.4	21.4	41.5	6.2	41.6	1.69	0.20	23.2	21.2	15.0	17.3	[91]
	-	27.59	-	-	-	-	-	-	-	29.93	10.94	11.64	-	[52]
	-	-	-	-	41.59	6.18	50.46	1.67	0.10	-	-	-	17.83	[92]
	11.07	16.24	61.73	10.96	48.70	0.75	48.39	1.19	0.97	-	-	-	12.48	[93]
Coconut	8.27	0.71	77.19	22.1	50.22	5.7	43.37	0	-	-	-	-	20.50	[94]
shell	8.21	0.1	73.09	18.6	48.63	6.51	44.64	0.14	0.08	19.8	-	30.1	-	[54]
	5.56	1.80	70.82	21.8	40.08	5.22	54.31	0.22	0.17	-	-	-	19.4	[95]
	6.88	2.78	81.65	15.57	46.33	5.93	42.05	1.98	0.93	31.06	30.93	32.44	18.2	[96]
	-	1.02	83.01	15.97	50.34	6.26	42.08	0	0.31	-	-	-	20.24	[87]
	10.70	0.56	79.18	20.26	47.94	6.41	45.56	0.10	-	-	-	-	17.35	[97]
	10.1	3.2	75.5	11.2	64.23	6.89	27.61	0.77	0.50	17.89	56.29	25.82	20.15	[98]

\*Obtained experimentally

\*\*Predicted through correlations (Friedl et al. [99])

*Continued on next page*

Biomass	Proximate analysis (%)				Ultimate analysis (%)					Lignocellulosic composition (%)			HHV (MJ/kg)	Author's	
	Moisture	Ash	Volatile matter	Fixed carbon	C	H	O	N	S	Cellulose	Hemicellulose	Lignin			
Palm kernel	10.50	2.46	65.42	21.62	47.90	6.13	45.55	0.55	-	45.69	6.41	47.90	16.83	[100]	
shell	4.7	7.2	74.3	13.8	49.7	5.3	44.8	0.8	0.2	-	-	-	12.24	[101]	
	9.4	6.7	82.5	1.4	44.56	5.22	49.77	0.4	0.05	33.04	23.82	45.59	15.6	[102]	
	21.4	4.38	-	-	46.68	5.86	42.01	1.01	0.06	-	-	-	19.78	[103]	
	7.96	1.1	72.47	18.7	50.01	6.85	41.15	1.90	-	29.7	-	53.4	-	[54]	
	-	2.05	75.21	22.74	50.73	5.97	40.83	0.36	0.06	-	-	-	20.35	[104]	
	7.52	2.67	69.35	20.46	46.05	5.164	45.40	0.62	0.14	14.64	27.06	58.30	18.96	[105]	
	12.69	2.81	75.14	22.05	51.56	6.31	41.33	0.7	0.1	33.03	23.82	45.29	-	[106]	
	4.0	3.0	53.0	40.0	51.0	3.0	39.0	7.0	0	30.0	22.0	48.0	-	[107]	
	Sugarcane bagasse	51.01	3.20	83.66	13.15	45.48	5.96	45.21	0.15	-	-	-	-	18.73	[94]
		5.2	3.9	82.5	8.3	42.5	5.4	47.6	0.4	-	-	-	-	16.27	[82]
7.04		12.34	70.47	10.15	41.39	4.99	40.86	0.32	0.11	53.18	14.63	32.19	15.11	[105]	
-		4.70	81.20	8.06	39.92	5.16	49.94	0.24	0.036	32.57	23.48	15.83	16.47	[108]	
2.80		6.75	80.32	10.14	47.40	6.14	46.18	0.28	<0.1	-	-	-	18.51	[22]	
-		-	-	-	32.5	5.01	0.56	0.38	61.55	36.9	26.3	19.2	16.53	[109]	
-		-	83.3	-	43.06	5.51	51.28	0.05	0.10	-	-	-	16.05	[21]	
-		3.55	-	-	39.78	5.32	50.98	0.37	0	48.45	29.92	17.12	17.10	[110]	
-	5.6	86.6	13.4	44.2	5.8	49.7	0.2	-	43.4	-	-	14.4	[111]		

In Tabasco, some strategies are being implemented to maximize the energy valorization of wastes and minimize the environmental impact in the agroindustrial sector. In the sugar industry, it has been possible to meet their entire electricity demand through the combustion of residual biomass (bagasse and filter cake) from the sugarcane juice extraction process. The Santa Rosalía de la Chontalpa Sugar Mill, part of the Beta San Miguel® Group, in Cardenas, Tabasco, has installed gas purification systems to mitigate emissions from combustion, and uses by-products obtained through composting [112]. Similarly, in the palm oil industry, various processing byproducts are used: fiber is used as a fuel source in boilers for steam generation, and rachis and ash are employed in composting processes. The fruit fiber, ash, rachis, and palm kernel shells are reintegrated into the plantations [113]. These sustainable biomass waste management strategies are implemented by Oleopalma®. These examples illustrate that residual biomass generated in the agroindustry in Tabasco is recurrently used as an alternative fuel source. However, other biomass resources could represent significant potential in bioenergy production. Despite the large territorial extension of this economic sector, there is limited development in the creation of value-added products such as biofuels or bioproducts.

Therefore, we aim to evaluate the bioenergetic potential of five agricultural-agroindustrial wastes generated in the state of Tabasco, Mexico. Cocoa pod husk, coconut shell, banana rachis, palm kernel shell, and sugarcane bagasse wastes were selected for this study since their crops represent 83.4% of agricultural production and 48.6% of the total crop area in Tabasco, Mexico. The elemental content (CHONS) of the wastes was determined and used in four correlations from the literature to indirectly determine the bioenergetic content. These indirect results were then compared with direct determinations using a bomb calorimeter. The heavy metal content was assessed to evaluate the potential use of the biomasses as alternative fuels, considering the maximum permissible limits for biomasses. A completely aleatoric two-factor factorial design (type of waste and different calorific value estimation methods) was used, each with five levels ( $5 \times 5$ ). Additionally, the yield in kilograms of wastes generated per kilogram of production was estimated for each crop. Finally, the bioenergetic potential of the agricultural and agroindustrial sector in the state of Tabasco, located in southeastern Mexico, was assessed through its five major crops.

## 2. Materials and methods

### 2.1. Biomass collection and preparation

Coconut shell (*Cocos nucifera* L.), palm kernel shell (*Elaeis guineensis*), banana rachis (*Musa paradisiaca* L.), sugarcane bagasse (*Saccharum officinarum* L.), and cocoa pod husk (*Theobroma cacao* L.) were employed as biomass samples based on the agricultural review of the state of Tabasco, whose crops represent most of the state's production and crop area [5]. These samples were sourced from various locations within Tabasco, Mexico as detailed in Table 3. Before characterization, the samples underwent a pretreatment drying phase. Subsequently, they were ground using a semi-industrial electric shredder and sieved with a #40 and #10 mesh screens to achieve a particle size below 2 mm.

**Table 3.** Source of biomass and type of production or product.

Crops	ID	Source	Type production/product
Sugarcane	BC	“Santa Rosalía de la Chontalpa” Sugar Mill, Cárdenas	Sugar, molasses
Cocoa	CCa	Cocoa farm “Villa Aldama”, Comalcalco	Seeds
Coconut	CCo	Local Agricultural Association of Coconut Producers, Paraíso	Copra
Oil palm	CPAc	Oleopalma®, Jalapa	Palm oil
Banana	PPI	Banana plantation “La platanera”, Cunduacán	Banana exportation

## 2.2. Proximate and ultimate analysis

The proximate analysis of the five biomasses was carried out according to ASTM D-2974 [114]. Moisture content was assessed by oven-drying the samples at 105 °C for 24 hours, volatile matter was determined at 550 °C for 2 h, and ash content was measured at 800 °C for 1 h. Ultimate analysis was performed in quadruplicate using a Perkin Elmer® PE2400 CHNS Elemental Analyzer ( $\leq 0.2\%$  precision) to measure the carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) content. The Oxygen (O) content was then calculated arithmetically using the following expression:

$$O(\%) = 100 - C - H - N - S - Ash \quad (1)$$

## 2.3. Higher heating value (HHV)

The HHV of the biomass samples was predicted using equations reported in the literature, based on the ultimate analysis data previously obtained. The predicted HHV of the biomass sample was then compared with the experimentally determined heating values obtained through bomb calorimetry. The bomb calorimetry analyses were performed in quadruplicate using an Automatic Isoperibol Calorimeter Parr® 6400 (0.1% precision), following the ASTM D5468-02 standard method. The experimental HHV was calculated using the Boie [115], Channiwala [94], Dulong [94], and Friedl [99] equations, as shown in Table 4.

**Table 4.** Predictive equations for higher heating value (HHV) from literature.

Equation	Fuel	Author
$HHV (MJ/kg) = [(0.3516 * C) + (1.16225 * H) - (0.1109 * O) + (0.0628 * N) + (0.10465 * S)]$	Biomass, coal, coke, char, oils	Boie [115]
$HHV (MJ/kg) = [(0.3491 * C) - (1.1783 * H) + (0.1005 * S) - (0.1034 * O) - (0.0151 * N) - (0.211 * Ash)]$	Gaseous, liquid fuels, coals, chars, biomass, residue	Channiwala and Parikh [94]
$HHV (MJ/kg) = [(0.3383 * C) + [1.443 * (H - O/8)] + (0.0942 * S)]$	Coal	Dulong [94]
$HHV (kJ/kg) = [(3.55 C^2) - (232 * C) - (2230 * H) + (51.2 C * H) + (131 * N) + 20600]$	Biomass (wood, grass, rye, rape, reed, brewery waste, poultry litter)	Friedl et al. [99]

## 2.4. Ash-free calorific value (AFCV)

To quantify the calorific value of the studied biomasses more precisely, an adjustment was implemented to discriminate the influence of the non-combustible fraction represented by ashes. This adjustment consisted of calculating the ash-free calorific value (AFCV) using the experimental calorific values of each biomass sample, based on the equation proposed by Wang et al. [116]:

$$AFCV = \frac{100 * \text{calorific value}}{100 - Ash} \quad (2)$$

## 2.5. Experimental design

A completely randomized two-factor factorial design was used: Type of waste and different calorific value estimation methods, each with five levels ( $5 \times 5$ ) with four replicates per factor, obtaining 100 interactions. The wastes used to estimate their calorific value were: BC, CPAc, CCa, CCo, and PPl. The indirect calorific values were determined using equations developed by authors such as Boie, Channiwala, Dulong, and Friedl, which are based on elemental content. A direct method using a bomb calorimeter was included. The response variable was the calorific value in units of MJ/kg.



## 2.6. Statistical analysis

Since the data complied with the assumptions of normality and homoscedasticity, a factorial analysis of variance (ANOVA) with interaction was conducted, followed by a multiple comparisons Least Significant Difference (LSD) test.

## 2.7. Mean Absolute Error (MAE) and Mean Bias Error (MBE)

To assess the correlation between the predicted and experimentally determined HHV, both data sets were compared. Two statistical parameters of estimation error were employed: The Mean Absolute Error (MAE) and the Mean Bias Error (MBE) [117], calculated as follows:

$$MAE = \frac{1}{n} \sum_{i=1}^n \left| \frac{HHV_{predicted} - HHV_{experimental}}{HHV_{experimental}} \right| * 100\% \quad (3)$$

$$MBE = \frac{1}{n} \sum_{i=1}^n \left[ \frac{HHV_{predicted} - HHV_{experimental}}{HHV_{experimental}} \right] * 100\% \quad (4)$$

The accuracy of a correlation is evaluated by MAE, which compares the predicted and experimental HHVs. A lower MAE value indicates a higher level of accuracy. The correlation with the lowest MAE value demonstrates the best agreement between the estimated and experimental HHV, resulting in the most accurate predictions.

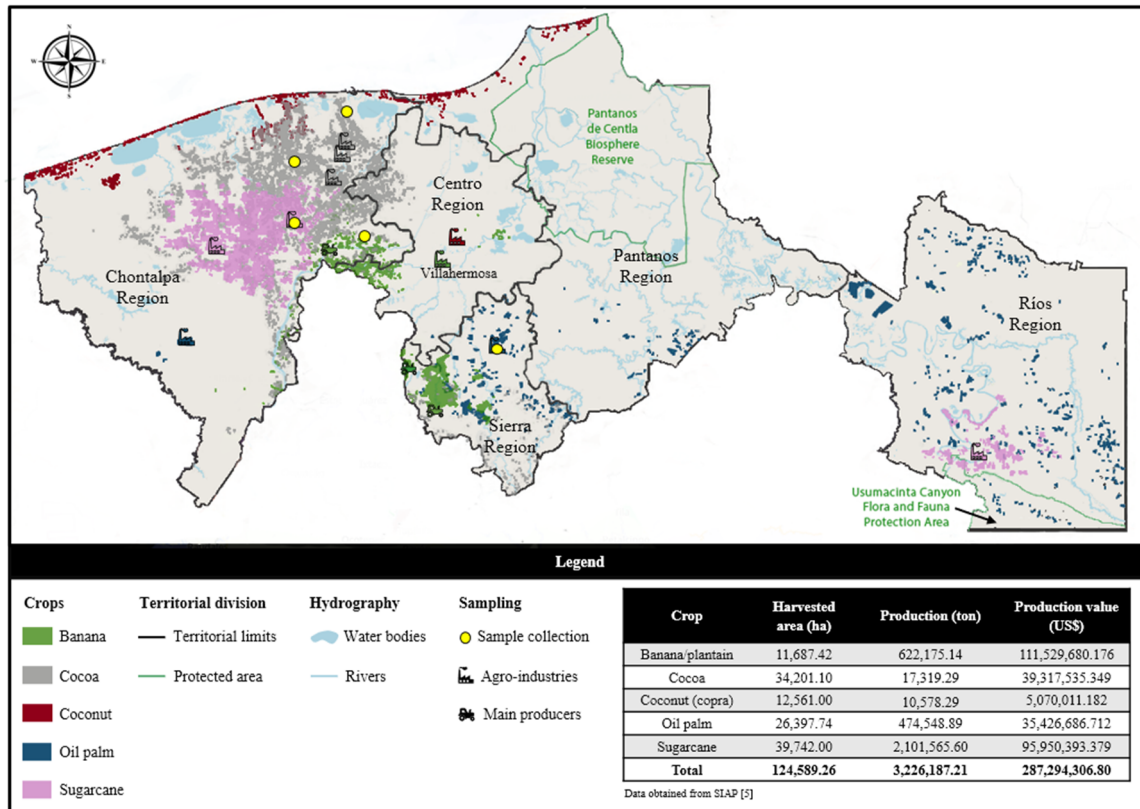
The MBE, on the other hand, can either have a positive or negative value. A positive MBE indicates an overall overestimation, while a negative value denotes an overall underestimation of the sample population. The magnitude of the MBE reflects the level of bias in the correlation. The accuracy of the correlations can be determined by the proximity of the MBE value to zero, regardless of its positive or negative sign.

## 2.8. Heavy metal content analysis

All biomass intended for fuel must be characterized for its heavy metal content due to the high risk of atmospheric contamination. The metal content was characterized following the US EPA 6010B method [118] using an Inductively Coupled Plasma (ICP) Atomic Emission Spectrometer, Optima 5300 PerkinElmer® ( $\leq 5\%$  relative standard deviation). The results were compared with the maximum permissible limits (MPL) established in ISO 17225-1:2014, which is used for solid biofuels. These analyses were conducted at Geocycle® coprocessing laboratory located in Macuspana, Tabasco.

## 3. Results and discussion

Figure 1 shows the distribution of coconut, cocoa, banana, sugarcane, and oil palm crops across the five geographical regions of Tabasco state: Centro, Chontalpa, Pantanos, Sierra, and Ríos. It is observed that the Chontalpa Region is where the largest amounts of these crops are located and the smallest amounts are in the Pantanos Region and the Center Region. Figure 1 also indicates the locations of sample collection points, existing processing facilities (agro-industries), and the major agricultural producers. Additionally, it provides information on the yields generated by each crop in the region.



**Figure 1.** Sampling locations of agricultural wastes from crop plantations in Tabasco, Mexico.

The limited agricultural and agroindustrial development in the Pantanos region is due to the presence of the Pantanos de Centla Biosphere Reserve. Additionally, the high population density and consequent urban development in the Centro region result in limited availability of land suitable for agriculture.

Figure 1 shows that sugarcane cultivation covers the largest territorial extension, with 39,742 ha and a production of 2,101,565.60 ton and generates a production profit of US\$95.95 million in the year 2022, making it the most industrialized agricultural product in Tabasco. This is reflected from the presence of three sugar mills in the state. The cocoa cultivation is an emblematic crop of great importance worldwide, originally from Tabasco. This crop has the second largest extension with 34,201 ha and a production of 17,319.29 ton/year, generating a profit per production of US\$39.32 million. However, despite the presence of three chocolate processing plants, the level of cocoa industrialization is very low, with most of the state's production distributed regionally and nationally at the bean level.

Oil palm is a crop that covers a territorial extension of 26,397.74 ha and a production of 474,548.89 ton/year. That crop has surged in the last two decades, exist two palm oil extraction plants installed, and a third plant will be installed. Coconut cultivation is distributed along the entire coastal strip of Tabasco state (12,561 ha). Although the conditions in this area are ideal for its development, coconut production is the lowest among the crops in this study 10,578.29 ton, generating a profit per production of US\$5.07 million. In terms of industrialization, there is only one coconut oil extraction plant, located in the state capital, which is at a very considerable distance from the producing area (Figure 1).

The banana crop has the highest economic value (US\$111.53 million) in this work although it has the second highest production (622,175.14 ton/year). This cultivation has a fundamental role in the economy of Tabasco. However, its industrialization in the region is limited by the scarce presence of processing plants, with most of the product being exported both nationally and internationally at the fruit level.

These five crops cover a territorial extension of 124,589.26 ha (5.04% of the territorial extension of Tabasco state), a production of 3,226,187.21 ton/year, and generate a profit per production of US\$287.29 million. Table 5 provides an estimate of the amount of waste generated by each crop, determined based on the biomass discarded about to the total crop production from different literature references.

**Table 5.** Estimation of waste per crop.

Crop	Production 2022 year (ton)	Biomass	$\text{kg}_{\text{biomass}}/\text{kg}_{\text{crop production}}$	Waste (ton)
Sugarcane	2,101,565.60	Sugarcane bagasse	0.2857 [20]	600,417.29
			0.28 [52]	588,438.37
			0.2828 <sup>a</sup>	594,322.75 <sup>b</sup>
Oil palm	474,548.89	Palm kernel shell	0.06 [23,24]	28,472.93
			0.059 [119]	27,998.38
			0.0595 <sup>a</sup>	28,235.66 <sup>b</sup>
Cocoa	17,319.29	Cocoa pod husk	0.70 [52]	12,123.50
			0.67 [15]	11,603.92
			0.685 <sup>a</sup>	11,863.71 <sup>b</sup>
Banana	622,175.14	Banana rachis	0.16 [16]	99,548.02 <sup>b</sup>
Coconut	37,779.61 <sup>c</sup>	Coconut shell	0.12 [18,19]	4,533.55
			0.15 [17]	5,666.94
			0.135 <sup>a</sup>	5,100.25 <sup>b</sup>

<sup>a</sup>average

<sup>b</sup>calculated waste

<sup>c</sup>equivalent to the percentage that copra represents (0.28%) of the total fruit

Cocoa is the crop that generates the largest amount of waste per unit of production (0.685  $\text{kg}_{\text{biomass}}/\text{kg}_{\text{crop}}$ ), followed by sugarcane (0.2828  $\text{kg}_{\text{biomass}}/\text{kg}_{\text{crop}}$ ), banana (0.16  $\text{kg}_{\text{biomass}}/\text{kg}_{\text{crop}}$ ), coconut (0.135  $\text{kg}_{\text{biomass}}/\text{kg}_{\text{crop}}$ ), and oil palm (0.0595  $\text{kg}_{\text{biomass}}/\text{kg}_{\text{crop}}$ ). Based on these waste generation rates relative to production, it is estimated that sugarcane bagasse is the biomass with the greatest generation capacity in Tabasco (594,322.75 ton), followed by banana rachis (99,548.02 ton), palm kernel shell (28,235.66 ton), cocoa pod husk (11,863.71 ton), and coconut shells (5,100.25 ton). Considering the sum of the estimated waste averages, a potential of approximately 739,070.39 tons of biomass per year is estimated, of which 80.4% has evidence of utilization, such as sugarcane bagasse in sugar mills.

Table 6 summarizes the characteristics of the target biomasses, organized into agricultural and agroindustrial categories. The components derived from proximate and ultimate analyses are presented.

**Table 6.** Comprehensive characterization of biomass samples.

Characteristics	Agricultural			Agroindustrial	
	CCa	CCo	PPI	BC	CPAc
<b>Proximate analysis (%)</b>					
Moisture	83.20 ± 0.77	13.85 ± 0.68	90.406 ± 0.421	16.46 ± 4.77	20.47 ± 3.73
Ash	19.732 ± 0.31	1.330 ± 0.58	25.923 ± 0.75	12.139 ± 0.63	11.290 ± 1.89
Volatile matter	70.509 ± 2.88	87.667 ± 2.94	69.829 ± 4.03	87.861 ± 0.89	81.069 ± 1.78
Fixed carbon	9.759 ± 1.75	11.0 ± 1.67	4.247 ± 4.52	*	7.641 ± 0.65
<b>Ultimate analysis (%)</b>					
C	48.327 ± 2.62	48.340 ± 0	39.093 ± 0.53	45.440 ± 0.26	51.387 ± 0.58
H	5.777 ± 0.44	5.263 ± 0.01	4.747 ± 0.07	5.643 ± 0.02	5.713 ± 0.03
O	24.13 ± 2.71	43.97 ± 0.51	28.593 ± 0.17	35.48 ± 0.89	30.15 ± 2.44
N	1.797 ± 0.48	1.083 ± 0.07	1.577 ± 0.14	1.267 ± 0.05	1.310 ± 0.17
S	0.233 ± 0.31	0.03 ± 0	0.060 ± 0.08	0.013 ± 0.03	0.183 ± 0.03

\*Not identified

The proximate analysis indicates a lower moisture content for most biomasses, except for PPI (90.40%), which is upper than the limits established by ISO 17225-6. This standard requires a moisture content of  $\leq 12\%$  for energy recovery, a value representative of non-wood biomass pellets, such as those analyzed in this study. The fixed carbon values obtained were similar to those summarized in Table 2 for materials such as CCA and CCo. However, slightly lower values were observed for PPI and CPAC biomasses.

Regarding ash content, CCo recorded the lowest value with 1.330%, while PPI had the highest with 25.923%. This difference is significant since high ash content can reduce the calorific value of the material, as reported by Sosa et al. [120]; the authors indicated that the high presence of ash or mineral material significantly reduces the calorific value of the biomass. Moreover, a high volatile matter content in biomasses, such as BC and CCo (87.861% and 87.667%, respectively), suggests a greater potential for their utilization in bioenergy production, especially in the form of biogas.

The ultimate analysis (Table 6) indicates that CPAC presents the highest carbon (C) content (51.387%) among the analyzed biomasses, similar to the findings of Ma et al. [106] and Chang et al. [104]. In contrast, Liew et al. [107] reported a hydrogen (H) content of 3.0%, which is significantly lower than the value obtained in this study (5.713%). However, it is important to highlight that their results were presented on a “dry ash-free basis”. Regarding oxygen (O) content (30.15%), several authors mentioned in the literature review (Table 2) indicate comparatively higher values (39.0–49.77%).

CCo presents carbon (C) values (48.340%) similar to those of BC and CCA (Table 6). However, Rout et al. [98] reported a higher C content for CCo (64.23%). Regarding the oxygen (O) content, CCo shows the highest value (43.97%) among the analyzed biomasses, while Kabir Ahmad et al. [95] obtained a value of 54.31%, and Rout et al. [98] recorded a lower value of 27.61%. These differences may be attributed to the use of different techniques and equipment, as well as the different particle sizes employed in this study.

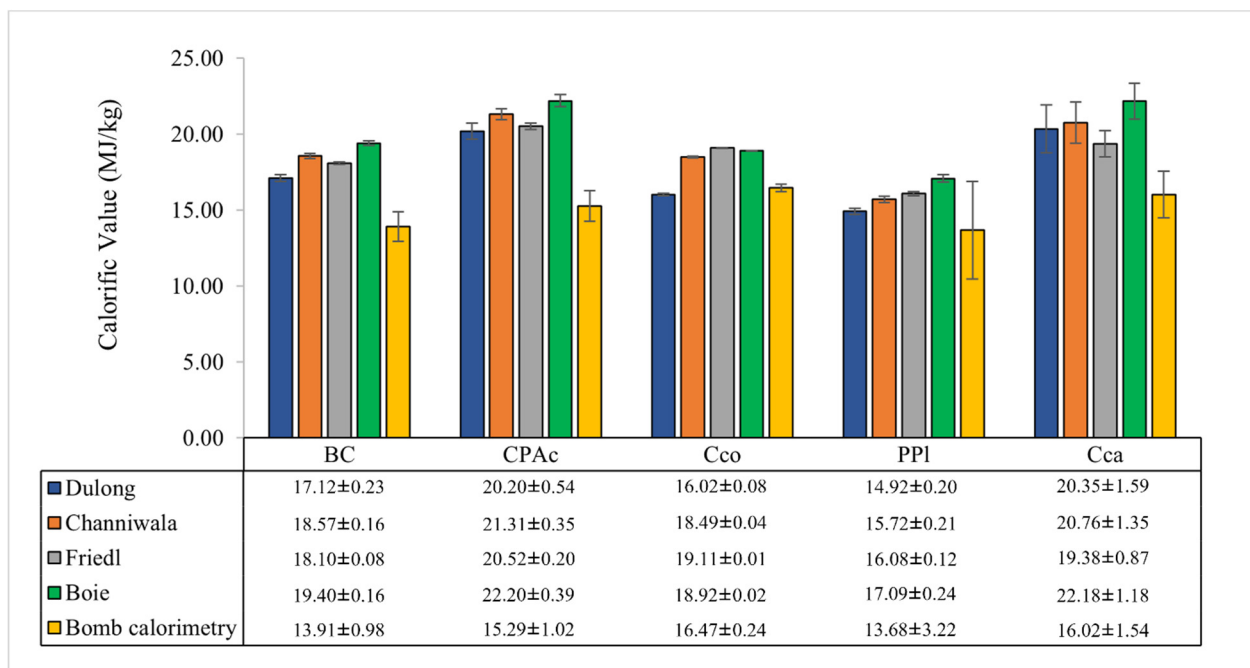
PPI has the lowest hydrogen (H) and carbon (C) content (4.747% and 39.093%, respectively) compared to the other biomasses analyzed, similar to what was reported by Granados et al. [82] and Balogun et al. [84]. Additionally, PPI has the second lowest oxygen (O) content (28.593%), and it shows a lower value compared to 36.4% from Granados et al. [82].

Adjin-Tetteh et al. [93] reported very low hydrogen (H) values (0.75%) for CCA (Table 2), while in the ultimate analysis, the H content is 5.777%. Oxygen (O) is observed to have the lowest value (24.13%) compared to the other biomasses and reported values (38.51–50.46%) (Table 2). This difference may be related to the processing method of their samples.

In relation to BC, Kanwal et al. [109] reported a considerably lower carbon (C) value of 32.5%, while in the ultimate analysis, there is a C content of (45.440%). Regarding oxygen (O) content, the results obtained in this study (35.48%) are remarkably low compared to those reported by other authors (40.86%), except for Kanwal et al. [109] who reported 0.56%.

Nitrogen (N) content ranges between 1.083–1.797%, and sulfur (S) content ranges between 0.013–0.233%. For both elements, the highest content is found in CCA, while the lowest N content is in CCo, and the lowest S content is in BC.

Figure 2 shows the comparison of the HHV values calculated indirectly by the four stoichiometric equations and directly by the bomb calorimeter.



**Figure 2.** Comparison between predicted and experimental HHV of the samples.

It can be observed that CCo and CCa have the highest experimental calorific values (16.47 MJ/kg and 16.02 MJ/kg, respectively), followed by CPAc, BC, and PPI (15.29 MJ/kg, 13.91 MJ/kg and 13.68 MJ/kg, respectively). This coincides with previous studies that have reported similar results for CCa, CPAc, PPI and BC [84,89,100,108]. Nevertheless, the CCo results (17.35–20.498%) differ significantly from those obtained in this work. These differences may be related to differences in carbon (C), hydrogen (H), oxygen (O), and ash content. Higher contents of C and H imply a higher biomass energy content, while an increase in O and ash content can lead to a decrease in HHV [115,121].

According to the ultimate analysis performed, PPI has the lowest carbon (C) and hydrogen (H) content (39.093 and 4.747%, respectively) compared to the other analyzed biomasses, and it has the lowest calorific value of these with 13.68 MJ/kg, validating the results of Sheng et al. [115]. In relation to the oxygen (O) content, CCo presents the highest value of all the analyzed biomasses (43.97%); however, it has the highest calorific value of these (16.47 MJ/kg), which does not agree with the results of Demirbas [121] and with those of several other researchers.

Regarding the ash and moisture content, an evident inverse correlation is observed between these properties obtained in this study and the calorific values obtained in the evaluated biomasses. CCo has the lowest moisture and ash contents of the five biomasses (13.85 and 1.330%) and obtained the highest calorific value of these (16.47 MJ/kg), while PPI has the highest moisture and ash contents of the five biomasses (90.406 and 25.923%) and obtained the lowest calorific value of these (13.68 MJ/kg), agreeing with the results of Demirbas [121].

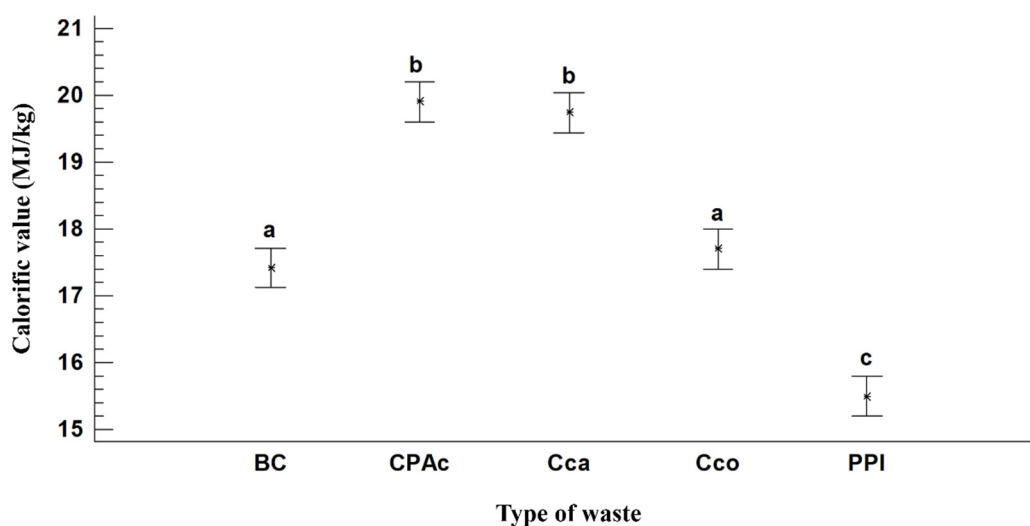
Therefore, the drying and cleaning processes are of great importance to reduce moisture and ash values, thereby achieving higher calorific values [122]. A high moisture percentage causes biomass to use a significant portion of its energy to evaporate the moisture, leading to incomplete combustion and the generation of carbon and carbon monoxide (CO), which results in less energy utilization [123]. Additionally, a high ash percentage decreases biomass combustion efficiency due to the presence of inorganic compounds [124]. The calorific values obtained after adjusting the ash content are shown in Table 7.

**Table 7.** Ash-free calorific value.

Ash-free calorific value				
BC	CPAc	CCo	PPI	CCa
15.833	17.232	16.691	18.473	19.960

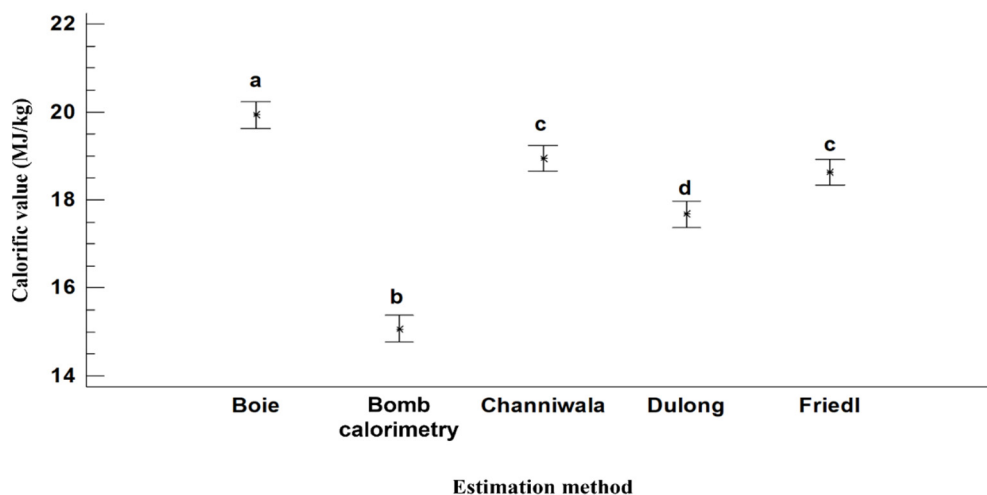
After adjustment, BC, CPAc, CCo, PPI, and CCa achieved increases in their calorific values of 1.14, 1.12, 1.013, 1.350, and 1.246%, respectively.

The factorial analysis of variance indicated a highly significant effect between the mean calorific values of the two factors, type of waste and calorific value estimation methods ( $P$ -value  $< 0.001$ ), with a confidence level of 95%. Regarding the type of waste, the multiple LSD comparison indicated that the wastes showing the highest calorific values are CPAc and CCa, with averages of  $19.904 \text{ MJ/kg} \pm 0.210$  standard error (SE) and  $19.738 \text{ MJ/kg} \pm 0.210$  (SE), respectively. CCo and BC obtained averages of  $17.701 \text{ MJ/kg} \pm 0.210$  (SE) and  $17.42 \text{ MJ/kg} \pm 0.2105$  (SE), respectively. PPI exhibited the lowest calorific value, averaging  $15.49 \text{ MJ/kg} \pm 0.210$  (SE) (Figure 3).



**Figure 3.** Average calorific values ( $\text{MJ/kg}$ )  $\pm$  standard error (SE) of type of waste. The multiple mean LSD comparison indicates statistically significant differences ( $P$ -value  $< 0.05$ ) denoted by different letters.

Regarding the calorific value estimation methods, the LSD comparison shows that the Boie correlation exhibited the highest calorific value with an average of  $19.92 \text{ MJ/kg} \pm 0.210$  (SE), followed by the Channiwalla and Friedl correlations with average values of  $18.948 \text{ MJ/kg} \pm 0.210$  (SE) and  $18.636 \text{ MJ/kg} \pm 0.210$  (SE), respectively. The lowest values were observed in the Dulong and bomb calorimetry determinations (Figure 4) with average values of  $17.675 \text{ MJ/kg} \pm 0.210$  (SE) and  $15.074 \text{ MJ/kg} \pm 0.210$  (SE), respectively.

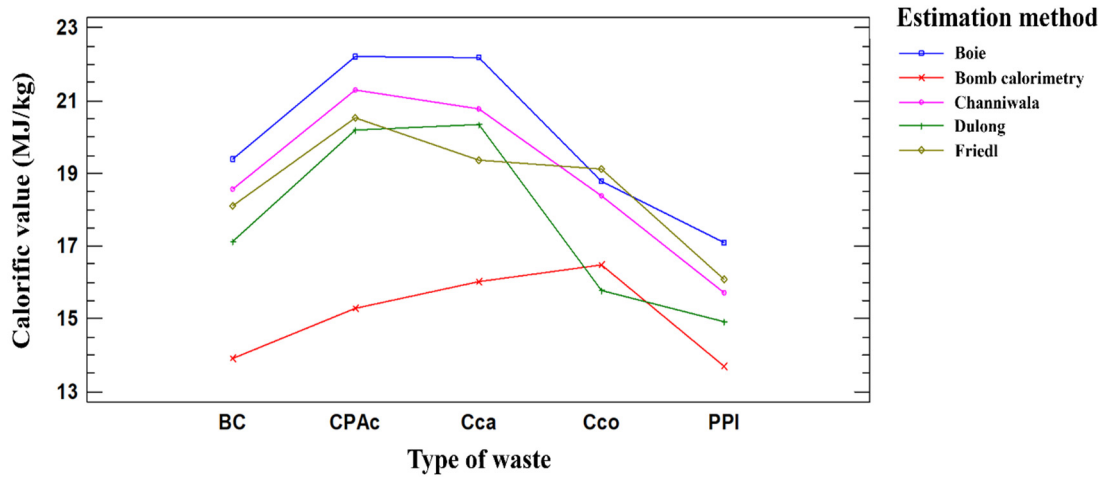


**Figure 4.** Average calorific values (MJ/kg)  $\pm$  standard error (SE) of different calorific value estimation methods. The multiple mean LSD comparison indicates statistically significant differences (P-value < 0.05) denoted by different letters.

The analysis of variance indicated highly significant statistical differences (P-value < 0.001) in the interaction between the different wastes (BC, CPAC, CCA, CCo, and PPI) and estimation methods (Boie, Bomb calorimetry, Channiwala, Dulong, and Friedl) of calorific value (MJ/kg), with a confidence level of 95%. It is observed that as the different methods are evaluated in the BC and CPAC wastes, and there is an upward trend in the calorific value. Similarly, in CPAC and CCA wastes, except for two methods, there was a decrease in their trend. The indirect methods show a downward trend, unlike the direct method, for CCA to PPI.

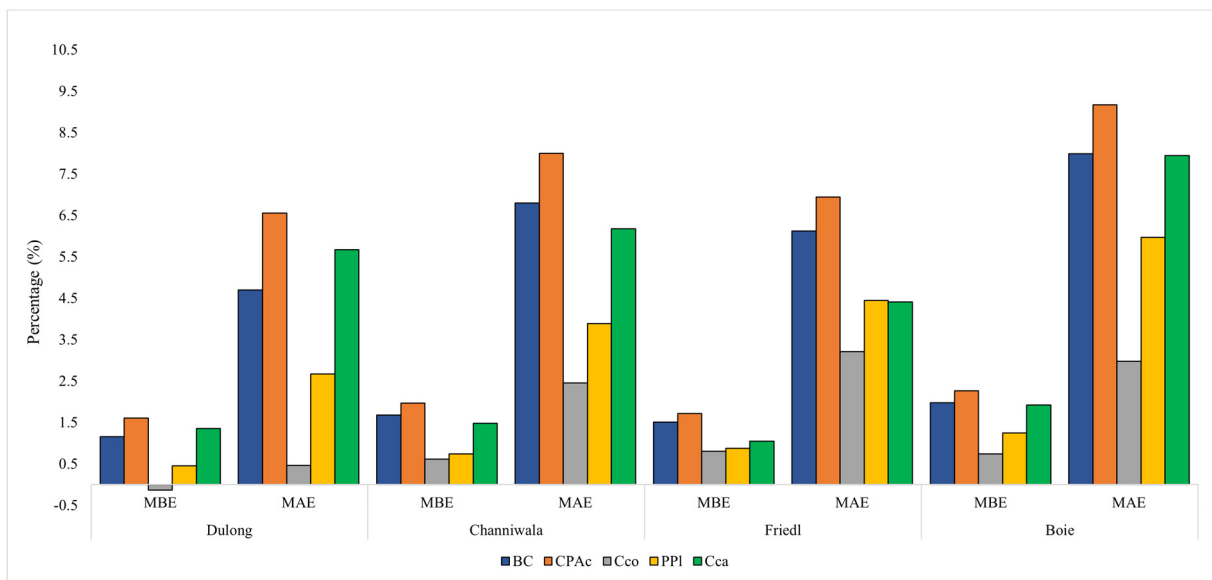
It is important to highlight that, although the direct method (Bomb calorimetry) shows the highest calorific value in CCo waste (16.47 MJ/kg  $\pm$  0.24 SE), this relationship is reversed when both methods are applied to PPI waste. In this case, the Bomb calorimetry method now predicts the lowest value, with 13.68 MJ/kg  $\pm$  0.470 SE, while the Dulong method shows a slightly higher value, with 14.92 MJ/kg  $\pm$  0.470 SE. It is relevant to emphasize the existing interactions, as interactions with the direct method represent similarities in the results obtained. Therefore, it is more desirable to obtain interactions between one of the indirect methods and the direct method (Bomb calorimetry).

When evaluating the Bomb calorimetry and Dulong methods in CCo waste, they estimate the calorific value in averages close to each other, with values of 16.46 MJ/kg  $\pm$  0.470 SE and 15.77 MJ/kg  $\pm$  0.470 SE, respectively. Despite this reversal, the values predicted by both methods do not differ significantly. Additionally, the calorific value estimation methods of Friedl, Boie, and Channiwala predict similarly for CCo waste, with averages of 19.11 MJ/kg  $\pm$  0.470 SE, 18.77 MJ/kg  $\pm$  0.470 SE, and 18.37 MJ/kg  $\pm$  0.470 SE, respectively. This pattern persists when evaluating these three methods in PPI waste, with average values of 17.08 MJ/kg  $\pm$  0.470 SE, 16.07 MJ/kg  $\pm$  0.470 SE, and 15.72 MJ/kg  $\pm$  0.470 SE, respectively. The Dulong and Friedl methods estimate similarly in CPAC waste, with average values of 20.51 MJ/kg  $\pm$  0.470 SE and 20.20 MJ/kg  $\pm$  0.470 SE, respectively (Figure 5).



**Figure 5.** Average calorific values (MJ/Kg) with the interaction of factors (estimation method and types of waste).

The MAE and MBE analyzed for each of the biomasses are shown in Figure 6. It is observed that the Dulong equation presented the lowest MAE for most of the wastes evaluated, except for CCa and CCo. This suggests that the values predicted by Dulong showed less deviation from the experimental values determined for these biomasses, meaning this equation provides the most accurate estimation of the experimental calorific value. Similarly, Dulong’s equation showed the lowest overestimation for biomasses, with an average value of 0.886%, in contrast to the 1.629% obtained from Boie’s equation. It is worth mentioning that Dulong’s equation was the only one that presented an underestimation for CCo, confirming the interaction between the methods observed in the factorial analysis in Figure 5.



**Figure 6.** Mean Absolute Error (MAE) and Mean Bias Error (MBE) for each method and wastes.

The metal content of the biomass samples is presented in Table 8.



**Table 8.** Heavy metal contents (mg/kg).

Metal	Limit (ISO 17225-1:2014) *	BC	CCa	CCo	CPAc	PPI
As	0.1–4.0	<10.0	≤10	≤10	≤10	≤10
Cd	0.03–5.0	<10.0	≤10	≤10	≤10	≤10
Cr	0.2–60.0	97.6	108.0	80.4	14.4	70.7
Hg	0.01–2.0	<1.0	<1.0	<1.0	<1.0	<1.0
Pb	0.1–30.0	<10.0	≤10	≤10	≤10	≤10
Zn	2.0–1600.0	106.5	332.5	53.7	18.8	164.9

\*Note: Based on the different types of biomass materials presents in the norm.

While the Cr concentrations in CPAc are the only ones below the limits specified by ISO 17225-1:2014, all the biomass samples exhibit concentrations lower than the stipulated limits for Hg, Pb, and Zn. In general, CPAc and CCo have the lowest content of heavy metals, followed by PPI, BC, and CCa.

There is interest in studying the energy potential of agricultural or agro-industrial waste. These materials are often integral to the energy self-sufficiency of certain countries [9] and they offer environmental benefits by substituting conventional fuels in activities such as electricity generation [10].

#### 4. Conclusions

The bioenergy capacity of the five agricultural and agroindustrial wastes generated in Tabasco, Mexico is significant. The elemental content was fundamental for performing the stoichiometric calculations using different predictive methods to determine the calorimetric value. Regarding the stoichiometric methods, the Dulong method presented the greatest similarity in the results compared to the direct method. The heavy metal content showed values within or very close to the maximum permissible limits for fuel biomasses, suggesting their viability for potential use as alternative fuels. However, greater robustness in characterizing these parameters is necessary to obtain more accurate results.

Although coconut shell residual biomass exhibits a high calorific value, as well as low contents of nitrogen (N), sulfur (S), ash, and moisture, positioning it as a potential energy source, its limited production at the industrial level represents an obstacle to its direct use within the production processes of this crop. However, it is worth highlighting other industrial facilities, such as sugar mills or cement kilns, which could incorporate this biomass as an energy input, substituting conventional fuels and potentially reducing the carbon footprint of industrial combustion processes.

Cocoa pod husks, which are produced in large quantities and have extensive crop areas, present high ash, N, S, and heavy metals contents, which must be considered when evaluating their use as fuel. Palm kernel shells, with considerable waste generation and crop extension, offer an additional advantage due to an already established industrial process for utilizing their energy yield.

Even though sugarcane bagasse is not the material with the highest calorific value among the evaluated biomasses, its high availability and the existence of an established industrial process for its energy use make it a viable and attractive alternative fuel. This contrasts with other biomasses that may exhibit higher calorific values but have much lower waste generation. However, it is important to note its content of heavy metals.

Although banana rachis is generated in large quantities, its high moisture and ash content, along with its low calorific value, make it less viable as an alternative fuel. Therefore, other alternatives for its valorization should be considered.

Finally, the results obtained from the general and energetic characteristics of five biomasses make four potential resources to be used in direct combustion systems as a first option. However, there is the possibility of using them in the agro-industrial facilities themselves and establishing networks between

the agricultural and agro-industrial sectors to maximize the use of biomass, which is under-exploited in the study region.

Some issues arising from this research are: Analysis of the cost per unit of energy (US\$/MJkg<sup>-1</sup>) of biomasses; testing the calorific values of biomasses in pilot tests; obtaining emission factors to study the environmental impacts of biomass use; and assessing the feasibility of replacing conventional fuels with biomass to focus on real agroindustrial processes in the region.

### Use of AI tools declaration

The authors declare they have not used Artificial Intelligence (AI) tools in the creation of this article.

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### Conflict of interest

The authors declare no conflict of interest.

### Author contributions

Nathaly Alejandra Díaz Molina (ORCID: <https://orcid.org/0009-0003-3015-8474>). Undergraduate student, performed the characterizations, indirect calorimetric method calculations and literature review.

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Donato Antonio Figueiras: Laboratorian, performed the heavy metal content analysis and direct calorimetric method calculations. donato.figueiras@geocycle.com.

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