Evaluation of Lignocellulosic Biomasses for Pyrolysis Product Generation

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This study aimed to assess agroindustrial residues, namely acerola seeds, poultry litter, bean pods, corn cobs, coconut fiber, pine nut shells, peanut shells, pine, and passion fruit, for the production of pyrolysis products, thereby adding value to these environmental assets. The characterization of these biomasses was carried out through elemental analysis (CHN), thermogravimetry (TG), higher heating value (HHV), ash content, and protein content determination. The samples exhibited low ash content (1.04% to 11.92%), protein content (1.22% to 15.06%), and moisture content (7.82% to 15.31%). Thermogravimetric analysis revealed that compound degradation occurred between 115°C and 500°C, with higher heating values (16.73% to 19.94 MJ.kg^{-1}), indicating strong applicability in pyrolysis processes.

Keywords: Characterization. Pyrolysis. Agroindustrial Residue.

Introduction

Environmental pollution and the energy crisis resulting from using fossil fuels have driven the development of clean and renewable energy alternatives [1-5]. One such alternative is the utilization of biomass, which encompasses any renewable resource derived from organic matter of animal or plant origin found in nature or generated by humans and/or animals [1]. Lignocellulosic waste has been identified as an attractive feedstock for fuel production due to its potential for zero CO_2 emissions, abundant availability, and low cost. Biofuel is considered carbon-neutral and has garnered attention as a potential renewable energy source, alongside its capacity to mitigate greenhouse gas emissions [6-8]. Consequently, the biomass composition is crucial in assessing the generated products and their properties.

Lignocellulosic biomass resources can be utilized cleanly and efficiently through appropriate conversion techniques. One such technique is pyrolysis, which is employed for the efficient transformation of biomass, resulting in the production of numerous products (Table 1).

Depending on the characteristics of the samples, the pyrolysis products can be gas, liquid, or char. Thus, this study aims to characterize 9 different biomass sources.

Materials and Methods

Sample Preparation

Nine different biomass sources were employed in this study: acerola seeds (ACE), poultry litter (CF), bean pods (FEI), corn cobs (Mi.S), pine nut shells (PIN), peanut shells (AMD), pine bark (PNU), passion fruit peels (Ma.C) and coconut fiber (COC) (Table 2).

Method

Ash Content

The determination was performed by gravimetry in a muffle furnace, following the NREL/TP-510-42622 standard [18]. Porcelain crucibles were pre-weighed, and approximately 2 g of moisture-free samples were added. Triplicates were placed in the SPLABOR muffle furnace, model SP-1200, and heated to a temperature of 575 ± 25 °C for 4 hours. The samples were removed and transferred to a desiccator until they reached room temperature.

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Table 1. Applications of different types of pyrolysis.

Type	Process	Product	Reference
Animal fat	Catalytic Pyrolysis	Gasoline and diesel	[9]
Leather	Microwave-Assisted Pyrolysis	Liquid fractions and biochar	[10]
Bone	Pyrolysis and Co-pyrolysis	Biochar	[11]
Chicken feathers	Slow Pyrolysis	Biochar	[12]
Bovine manure	*In-situ* Catalytic Pyrolysis	Biogas	[13]
Tree leaves	Slow, fast, and microwave pyrolyzes	Biogas and biochar	[14]
Tree trunks and leaves	Intermediate Pyrolysis	Bio-oil and biochar	[15]
Tree branches	Co-pyrolysis	Biochar	[16]
Plant roots	Catalytic Pyrolysis	Biogasoline	[17]

Note: The references are listed with the author's names followed by the publication year.

Table 2. Biomass sources studied in this work.

Biomass	Acronym	Collection Location	Origin	Preparation
Acerola seeds	ACE	Aracaju/SE	Plant	Milling
Poultry litter*	CF	São Cristóvão/SE	Animal	Sorting
Bean pods	FEI	São Cristóvão/SE	Plant	Food Processor
Corn cobs	Mi, S	Vitória da Conquista/BA	Plant	Grater
Pine nut shells	PIN	Maringá/PR	Plant	Grater
Peanut shells	AMD	Malhador/SE	Plant	Milling
Pine bark	PNU	Commercial Sample	Plant	Milling
Passion fruit peels	Ma, C	Nossa Senhora do Socorro/SE	Plant	Grater
Coconut fiber	COC	Nossa Senhora do Socorro/SE	Plant	Grater

*With a usage batch (40 days in contact with the animals plus 15 days of sanitation gap), it is composed initially of wood shavings.

The calculation of the ash content was obtained using Equation 1 as follows:

$$\text{Ash Content (\%)} = \left(\frac{\text{Mass of Crucible with Ash} - \text{Mass of Crucible}}{\text{Sample Mass}}\right) \times 100 \qquad (1)$$

Elemental Composition (C, H, N, and O)

Elemental composition analysis was conducted using a Leco analyzer, Model CHN628, with helium (99.995%) and oxygen (99.99%) as gases and a furnace temperature of 950 °C. The equipment was calibrated using an EDTA standard (41.0% C, 5.5% H, and 9.5% N) with mass ranges between 10 and 150 mg to prepare the calibration curve. Approximately 50 mg of the sample was used for analysis in both cases. Tin foil was employed as a sample support for subsequent analysis. The percentage of oxygen was determined according to Equation 2 below [19]:

$$\%O = 100 - (\%C + \%H + \%N + \text{Ash Content } (\%)) \qquad (2)$$

in which: $\%C$ = carbon content; $\%H$ = hydrogen content; $\%N$ = nitrogen content.

The percentages of these atoms in the biomass can determine the molar ratios H/C and O/C, where the first parameter forms the abscissa axis in the Van Krevelen diagram, and the second parameter forms the ordinate axis.

Higher Heating Value (HHV) and Protein Content

HHV was calculated according to the following equation [20]:

$$HHV\ (MJ\ kg\text{-}1) = -1.3675 + (0.3137xC) + (0.7009xH) + 0.0318xO) \qquad (3)$$

in which HHV = Higher Heating Value; C = carbon content; H = hydrogen content; N = nitrogen content.

Protein content was determined following the NREL/TP-510-42625 methodology [21], and the equation below was applied:

$$\text{Protein Content } (\%) = \%N \times 6.25 \qquad (4)$$

in which $\%N$ is equal to the nitrogen content.

Thermogravimetric Analysis (TG)

TG analyses were conducted using the Simultaneous DTA-TG Apparatus, model DTA-50, manufactured by Shimadzu. The temperature range was set from 50 to 1000°C with a heating rate of 10°C/min under an inert atmosphere of N_2 at a 100 mL/min flow rate. A platinum crucible containing 5 to 10 mg of biomass was used for the analysis. The results were elucidated through the dTG curve, corresponding to the first derivative of mass change concerning temperature in the TG curve (dm/dT). This representation allows for easier visualization of information. Thus, the area under the peak corresponds to the mass variation [22].

Results and Discussion

Biomass Characterization

The samples exhibited less than 10% ash content, except for CF (11.92%) (Table 3). This higher value is attributed to the type of material used and the number of batches, leading to varying mineral concentrations being deposited [2,3]. Depending on the composition, ashes can function as catalysts, considering the target product [6]. This particular sample also displayed a higher heating value (HHV) of 16.73 MJ/kg, surpassing biomass sources like wood chips and eucalyptus bark, which are widely used in industrial boilers and have values of 16.46 and 13.92 MJ/kg, respectively [4].

CF also stands out for having the highest protein content in the dataset (15.06%). However, under these conditions, this biomass is unsuitable for industrial use due to the emission of toxic gases such as HCN, NOx, and NH_3. However, for the chemical and pharmaceutical industries, there is significant value depending on the compounds present, such as pyrrole, pyridine, and índole [5]. The calorific value can be assessed through the atomic ratio of O/C and H/C in the biomass using the van Krevelen diagram (Figure 2).

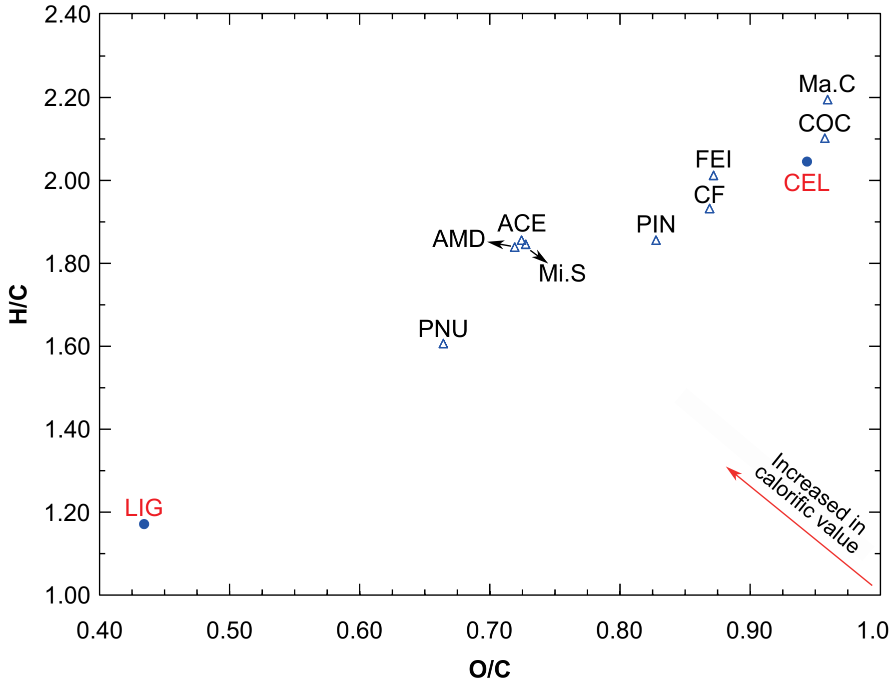
The ACE, Mi.S, AMD, and PNU samples exhibited high H/C and low O/C ratios, granting them the highest calorific value within the dataset. These samples also possess the lowest ash content, enhancing the thermal efficiency of the process and preventing reactor fouling [3]. The ACE, AMD, and Mi.S samples possess very close H/C ratios (1.86, 1.84, and 1.85, respectively). The same applies to the O/C ratio of these biomasses (0.72, 0.72,

Table 3. Higher heating value, protein content, and ash content of the biomasses.

Biomass	Acronym	Ash (%)	HHV (MJ/kg)	Protein (%)
Acerola seeds	ACE	2.71 ± 0.01	19.11	9.12
Poultry Litter	CF	11.92 ± 0.74	16.73	15.06
Bean pods	FEI	4.38 ± 0.06	17.60	7.91
Corn cobs	Mi.S	1.37 ± 0.13	19.44	5.86
Pine nut shells	PIN	3.88 ± 0.22	17.98	3.48
Peanut shells	AMD	2.76 ± 0.08	19.33	3.01
Pine bark	PNU	1.04 ± 0.13	19.94	1.22
Passion fruit peels	Ma.C	6.10 ± 0.32	16.79	8.03
Coconut fiber	COC	3.96 ± 0.11	17.22	3.29

Note: The values presented are mean values with associated standard deviations.

Figure 2. Van Krevelen diagram of the studied biomasses.



and 0.73, respectively), justifying the proximity of these data points on the graph. The remaining biomasses feature elevated molar H/C and O/C ratios, resulting in higher yields of volatiles and liquids and decreased energy conversion efficiency due to more significant CO_2 emissions from the higher O/C ratio [23]. High H/C ratios enhance the potential of using biomass for biofuel production, making it advantageous to incorporate feedstocks with these characteristics in thermochemical processes, thereby improving product quality [6].

Regarding the thermogravimetric analyses, when examining the events highlighted in Table 4, it is evident that the passion fruit peel biomass

Table 4. Temperature ranges and percentage mass loss of the samples.

	Moisture		Hemicellulose		Cellulose	
Samples	**ΔT (°C)**	**Mass Loss (%)**	**ΔT (°C)**	**Mass Loss (%)**	**ΔT (°C)**	**Mass Loss (%)**
ACE	27.00 – 114.00	7.82	221.00 – 298.00	14.05	305.00 – 403.00	27.15
Mi.S	31.68 – 77.78	7.94	259.06 – 304.29	29.36	346.42 – 379.89	28.51
AMD	29.00 – 110.00	8.01	250.00 – 409.00	50.11*	-	-
PNU	34.91 – 85.38	11.99	295.51 – 392.86	36.77*	-	-
Ma.C	32.19 – 76.94	15.31	208.77 – 257.85	21.62	298.59 – 331.67	18.60
COC	26.01 – 111.67	10.06	235.13 – 308.82	17.35	310.73 – 384.90	20.89
PIN	37.22 – 100.88	12.56	251.34 – 290.78	16.77	319.66 – 349.56	10.04
FEI	28.56 – 105.00	11.89	216.00 – 263.00	7.76	277.00 – 388.00	39.94
CF	39.94 – 115.96	10.59	267.68 – 353.27	42.00	437.67 – 486.51	6.41

Note: ΔT represents the temperature range in Celsius, and mass loss is expressed in percentage. *Demonstrated only an area corresponding to the temperature range of holocellulose.

exhibits the highest moisture content among the samples (15.31%). It also possesses the highest O/C ratio and the second-highest ash content (6.10%), which impacts its higher heating value (16.79 MJ/kg). However, this moisture percentage is considered low, and conditions, to the contrary, are not conducive to pyrolysis. Adequate thermal pre-treatment is recommended in such cases [7]. Each sample exhibited distinct temperature ranges for the degradation of lignocellulosic components (hemicellulose, cellulose, and lignin), considering their specific characteristics. In general, the degradation of compounds commences at around 115°C, concluding below 500°C. Above this temperature, no significant mass loss events are observed, enabling the assessment of pyrolysis of these biomasses for the production of bio-oil, biochar, or biogas.

Conclusion

A high O/C ratio and low protein, ash, and moisture content primarily characterize the analyzed biomasses. Thermogravimetric and elemental composition analyses reveal a higher calorific value than some biomasses already employed in combustion systems, showcasing their viability for pyrolysis processes to produce bio-oils. Characterizing these biomasses through GC-MS enables an assessment of their individual and/or combined applicability, contingent upon their chemical properties. This consideration encompasses a diverse range of industrial applications, including the food, pharmaceutical, cosmetic, fuel, and fine chemical industries.

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