Production and Characterization of Bio-Oil from Cassava Peel

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Agro-industrial residues are biomass of interest as they are energy sources and bioproducts with lower environmental impacts than traditional fossil fuels. Pyrolysis has been used to convert residual biomass into higher value-added products such as bio-oil. This work aimed to pyrolyze cassava peels to produce bio-oil and characterization using chromatographic techniques to obtain essential compounds for the chemical industry, adding value to this residue. The pyrolytic process generated 17.5% of bio-oil, with a high concentration of phenols and alcohols. Thus, this residual biomass has potential for industrial use, reducing the environmental impact of its deposit in landfills and offering industrial and economic benefits.

Keywords: Biomass. Bio-Oils. Chromatography Analysis. Pyrolysis.

Introduction

The global demand for energy and industrial inputs from renewable sources has led to a sustainable production and energy chain to replace non-renewable sources, such as fossil fuels [1].

Biomass stands out as a promising source of energy and bioproducts, considering its easy access and availability, low environmental impact with lower emissions of greenhouse gases, lower cost, and the reuse of various residues in their raw form [2,3]. Additionally, it positively impacts the generation of chemical products such as food and pharmaceutical inputs, surfactants, organic solvents, and fertilizers [4,5].

In developing countries, biomass is more abundant and consists of various materials, mainly agricultural residues. In Brazil, for example, tons of agro-industrial waste are generated annually [6].

The utilization of these residues is a highly relevant topic due to the large quantity of organic waste generated worldwide and the negative environmental impact of improper handling of these materials [7,8].

Cassava (*Manihot esculenta*) is a biomass of great interest and is one of the most popular crops in Brazil, cultivated in all regions of the country. One of its primary uses is to produce flour, and one of the central residues obtained during the beginning of this process is the peel [9,10].

According to the systematic survey of production (LSPA) from January 2022, conducted by the Brazilian Institute of Geography and Statistics (IBGE, 2022), the estimated production in Brazil is 18.03 million tons per year, cultivated on a total area of 1.24 million hectares [11].

Agro-industrial processes that use roots to produce flour generate large quantities of solid and liquid waste, including peels and pomace [12]. After pre-cleaning the peels, the leading industrial residue is produced, which usually lacks a sustainable destination and is disposed of in landfills [13].

The volume generated from this waste can reach up to 7.8% of the total harvested. If properly used, this waste can minimize environmental issues in the industry and, if commercialized, contribute to the production chain of cassava starch or flour and add profit to the sector [14].

One of the routes for reutilizing this waste is the pyrolysis process. Pyrolysis is a thermochemical conversion process that converts biomass into

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organic products of lower molecular complexity through thermal decomposition in an inert atmosphere, intending to generate higher-value products [15,16]. The process yields biochar (solid), non-condensable gases, and a condensable liquid fraction (bio-oil). The efficiency of the pyrolysis process depends on physicochemical parameters and the understanding of the properties of the biomass to be used in the process [17,16].

Bio-oil utilization is directly related to its physicochemical properties, particularly its chemical composition. Based on this composition, the produced bio-oil can have various applications in different areas, such as diverse chemical products like asphalt, pesticides, fertilizers, and pharmaceuticals, or directly as fuel in industrial boilers and gas turbines [18,19].

The most used analytical technique for characterizing bio-oil is gas chromatography (GC), typically coupled with spectroscopic methods such as mass spectrometry (MS) to provide further information about the chemical structure of the bio-oil components. A commonly used mass analyzer is the quadrupole, which is accessible and compatible with mass spectral libraries [20,21]. The work focuses on producing and characterizing bio-oil derived from cassava peel biomass. This biomass is an essential source of raw material.

Materials and Methods

Biomass Characterization

According to ASTM standard methods, biomass was characterized by proximate analysis [22,23]. Moisture was determined using a moisture analyzer (SHIMADZU, model MOC63u) at 140°C. The elemental analysis of the biomass was performed using a FlashEA 1112 Nitrogen and Carbon analyzer (Thermo Scientific), and the results were processed with CHN-628 v. 1.3 software. These results were then used to determine the biomass's High Heating Value (HHV). The determinations were performed by Sheng and Azevedo [24] according to the equation:

$$\boldsymbol{HHV}\ (\text{MJ kg-1}) = -\ 1.3675 + 0.3137.C + 0.7009.H + 0.0318$$

in which C, H, and O represent the percent weight of each element.

The thermal decomposition of the biomass was determined using a thermal analysis system (STA200RV, Hitachi, Japan), using a heating rate of 20 ºC min^{-1} till 900 °C under a flow of nitrogen gas. The weight loss of the sample was recorded as a function of temperature. The TGA results can be used to determine the different stages of the thermal decomposition of biomass.

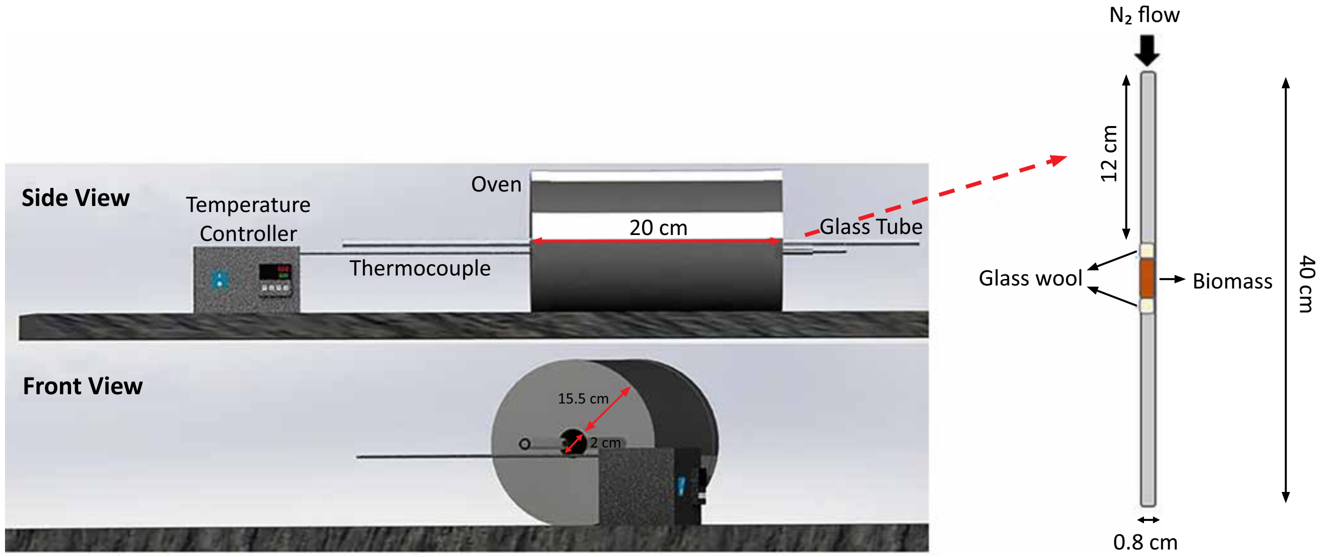
Pyrolysis Conditions

Fast pyrolysis experiments were conducted using a system consisting of a circular horizontal furnace with a diameter of 25 cm and a length of 20 cm. [25] The oven has an internal refractory layer with 11.5 cm of thickness and a central orifice with a diameter of 2 cm for introducing the glass reactor. The glass reactor has an inlet for inert gas (N_2). A thermocouple controls the temperature. Figure 1 (a, b) schematically illustrates the complete system and its detailed parts. The pyrolysis experiments were conducted at 600 °C, with a nitrogen flow rate of 2 mL min^{-1} and 0.1 g of biomass. The biomass was placed inside the reactor using glass wool at both ends [Figure 1 (b)]. The reactor containing the biomass was inserted into the preheated oven, ensuring that the biomass was centrally positioned for more uniform heating. The reactor was connected to the N_2 flow. The temperature was controlled so that the biomass inside the reactor reached 600 °C and remained at this temperature for 1 minute. Subsequently, the reactor was removed from the furnace, cooled to room temperature, and the bio-oil was eluted with 15 mL of acetone. Both bio-oil and biochar after solvent evaporation were weighted for mass yield determination.

Chromatographic Analysis – GC/qMS

Chromatographic analyses were performed using the GCMS-QP2010-Ultra model equipment

Figure 1. Pyrolysis system. (a) Oven, (b) reactor.



(a) Horizontal Cylindrical Oven **(b) Glass Reactor**

(Shimadzu, Japan). The capillary column was a DB-5, 60 m long, 0.25 mm internal diameter, and 0.25 µm stationary phase thickness. Helium was used as a carrier gas with a flow of 1 mL min^{-1}. In the splitless mode, sample injection (1 µL at a concentration of 5000 ppm) was performed using the AOC-20i automatic injector (Shimadzu, Japan). The system operated in SCAN mode. The oven was heated according to the following schedule: from 40 °C to 300 °C at 3 °C min^{-1}, remaining at this temperature for 10 min. Data treatment was performed using the GCMS solution software. The compounds were identified by retention index and mass spectra.

Results and Discussion

Biomass Characterization and Pyrolysis

Figure 2 presents the thermogravimetric profile of the biomass used in this study. The initial weight loss of 10.4% refers to the liberation of CO_2 and H_2O. The second significant event is the decomposition of cellulose and hemicellulose, which can not be differentiated. This weight loss begins at 160 °C (likely hemicellulose) and ends at 480 °C (probably cellulose), accounting for approximately 44,6% of total mass loss. Afterward, lignin decomposition occurs, corresponding to a loss of 14.1%.

Figure 3 displays the results of the preliminary biomass analysis and the pyrolysis mass yield. The sample shows a low moisture content, which is suitable for pyrolysis (< 10%). The volatile content was high (95.4%), while the ash and fixed carbon content were low. These results indicate the potential of this biomass to produce a higher content of bio-oil. The elemental composition highlighted the high percentage of oxygen (42.3%) related to bio-oil quality, which will probably be prosperous in oxygenated compounds like phenols, aldehydes, and ketones. Calculating the atomic ratios H/C (1.5) and the High Heating Value (HHV= 19.72 MJ kg^{-1}) are important energetic parameters for Cassava peel. H/C can be considered high for biomasses and indicates the presence of hydrocarbon-saturated chains due to the predominance of cellulose over lignin (which is more aromatic). HHV found is in accord with the literature [26].

The pyrolysis results for residual biomass show that bio-oil yield was 17.5%, but the amount of gases and the losses are very high. In a closed system, these gases could be reused to preheat

Figure 2. Profile obtained from the thermogravimetric analysis of the biomass.

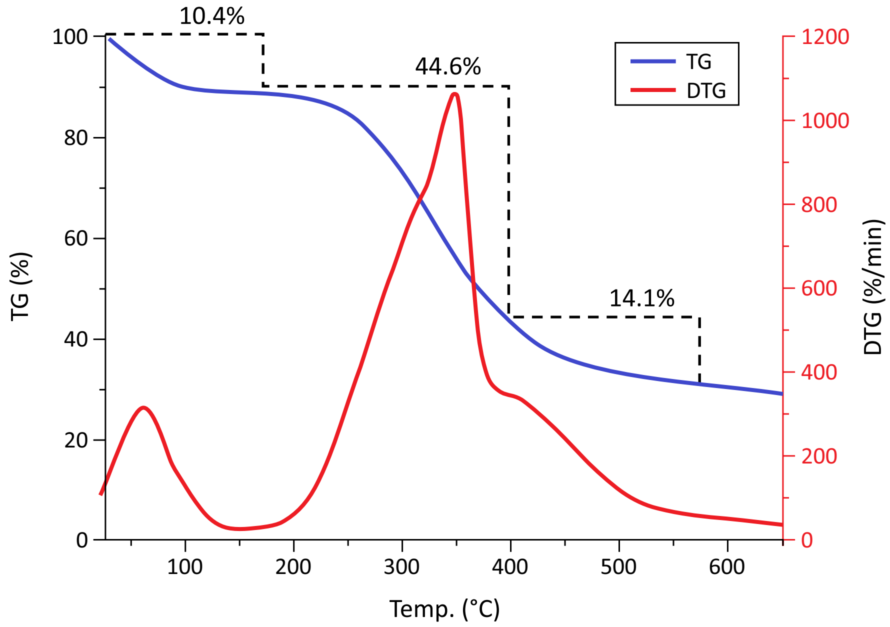
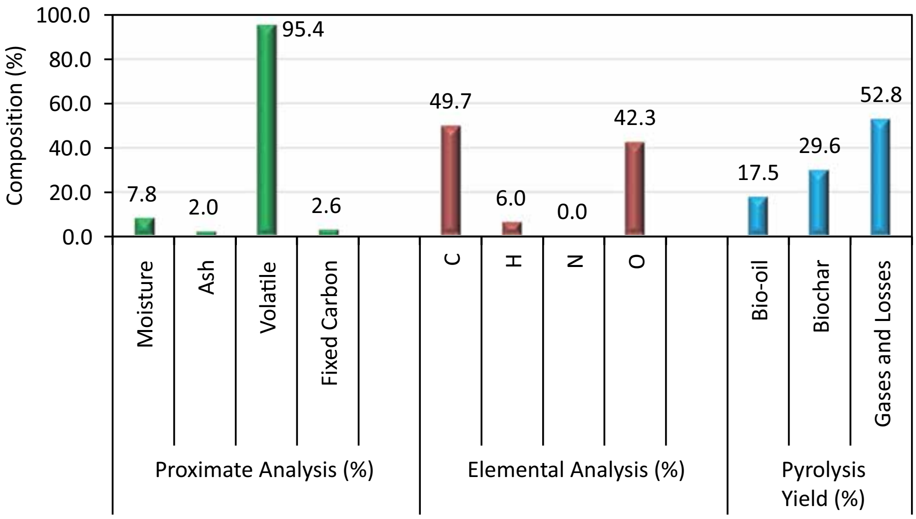


Figure 3. Preliminary analysis of the biomass and mass yield of the pyrolysis.



the system, which would not be considered a process loss. The loss of water and burning of gases leads to a substantial reduction in the residual volume of biomass (forming biochar with 29.6 % of the initial mass), which is an advantage of the pyrolytic process if considering the environmental impact of the significant number of residues deposited in landfills.

Bio-Oils Gas Chromatographic Analysis

Figure 4 shows the number of peaks and the percentage composition (related to the percentage area of each peak) of each class of chemical compounds found in the sample bio-oil. Table 1 shows the significant compounds in the analyzed cassava peel bio-oil.

Figure 4. Distribution of chemical classes found in the sample concerning percentage areas and peak numbers.

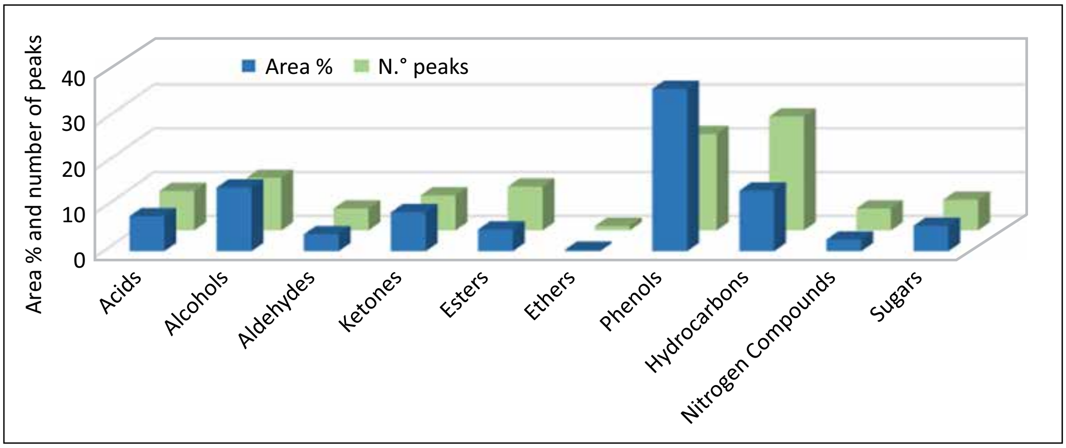


Table 1. Main compounds found in the analyzed bio-oil (area % ≥ 2.0%).

Chemical Classes	Compound Name	Area %
Acid	Oleic acid	2.00
Alcohols	1-heptacosanol	2.66
	1-octacosanol	2.2
Ketone	Acetovanillone	3.73
Sugar	Anhydrous sugar	2.06
Phenols	4-methyl catechol	4.20
	5-tert Butyl pirogalol	2.54
	4-methyl-syringol	2.43
	Isoeugenol	2.46
	4(1-propenyl)-syringol	2.4
	syringol	5.74

Phenols were the predominant class in terms of percentage area, followed by alcohol. Hydrocarbons and phenols presented the highest number of compounds (peaks). The presence of phenolic compounds, such as catechol and 4-methyl catechol, is appreciable, and they have a variety of applications, including photographic developer, dye developer for skins, intermediate for antioxidants in rubber and lubricating oils, polymerization inhibitors, and pharmaceutical products [27].

Phenolic compounds also have industrial and medical applications, replacing petroleum-derived compounds in producing phenolic resins. Compounds from other classes also have significant and diverse applications.

Conclusion

Cassava peel biomass exhibited expected results from elemental and proximate analyses, with yields viable for bio-oil production through pyrolysis. Chromatographic analysis has determined biomass to be highly suitable for producing bio-oil, which holds great potential for industrial applications. This promising solution helps minimize waste generation and reduces dependence on fossil fuels, thereby contributing to reducing carbon emissions in the atmosphere.

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