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Alteration of physico-chemical characteristics of coconut endocarp — *Acrocomia aculeata* — by isothermal pyrolysis in the range 250–550 °C

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ABSTRACT

Characteristics of the endocarp of *Acrocomia aculeata* fruit samples were evaluated before and after 2 h of isothermal pyrolysis in the range 250–550 °C. Differential thermogravimetric (DTG) curves from the char, obtained at 300 °C, confirm that degradation of hemicellulose and cellulose was complete and resulted in approximately 42.5% oxygen loss. The micrographs obtained from scanning electron microscopy with a field emission gun (SEM/FEG) confirmed a softened phase from the chars treated at 250 °C. The van Krevelen analysis shows that energy intensification of the sample transferred from peat to charcoal as the treatment intensity increased; this resulted in a 71% mass loss at 550 °C. The surface area of the treated sample increased exponentially with a factor of 1.2 per percentage of mass loss, from 450 °C and reached 216 m^2/g at 550 °C as a consequence of the development of microporous structures. The water-vapor-sorption properties were strongly affected by the treatment, with a pronounced type V isotherm curve for the char at 550 °C. These results show the evolution in chemical and structural properties of coconut endocarp during its isothermal pyrolysis. In particular, the improved char properties indicate that this material may be used as solid fuel or as raw material for the gasification process.

1. Introduction

The South-American palm species *Acrocomia aculeata*, commonly known as mbocayá, macaw, macauba or just coconut palm, has attracted the attention of researchers in recent years, mainly for its enormous potential as a sustainable source of feedstock for biorefinery [1–4].

Although *A. aculeata* is a native species of South America, its distribution spans the tropics and subtropics of Mexico and Central America as well. *A. aculeata* grows in regions that extend from Mexico to Argentina, but only in Paraguay, where 23 palm species have been identified [5], is its fruit (coconut) used commercially [6]; its many potential uses are shown in Fig. 1.

The endocarp represents about 21% of the overall residue mass generated after processing the mbocayá fruit [1]. In addition, it has higher values of fixed carbon, lignin content and energy density than other parts of the fruit [1,7]. These characteristic properties allow us to consider endocarp as potential feedstock to produce biofuel or materials like charcoal and activated carbon for a variety of applications; the thermochemical conversions, pyrolysis and gasification, could be promising methods to accomplish this.

During pyrolysis, thermal decomposition of biomass components (cellulose, hemicellulose and lignin) takes place. In general, the char produced is expected to have higher carbon content and heating value. Its chemical structure and physical properties such as density, specific surface area, water content, and electrical conduction, changes according to the pyrolysis conditions and feedstocks [8–10].

The characteristic properties of char indicate its different uses. Some important aspects that make it suitable as a solid fuel, adsorbent or as catalyst, are its hygroscopicity and specified surface area. When planning to use the char in a gasification process, in particular to obtain activated carbon or syn-gas, its porosity, moisture content and chemical composition, are important characteristics that result from the process, to maximize a particular product.

Adsorption experiments are considered a powerful tool to study materials. In previous studies [11,12], sorption properties were evaluated in torrefied biomass and bio-char obtained from wood samples. Natural fibers have displayed differences in water vapor sorption

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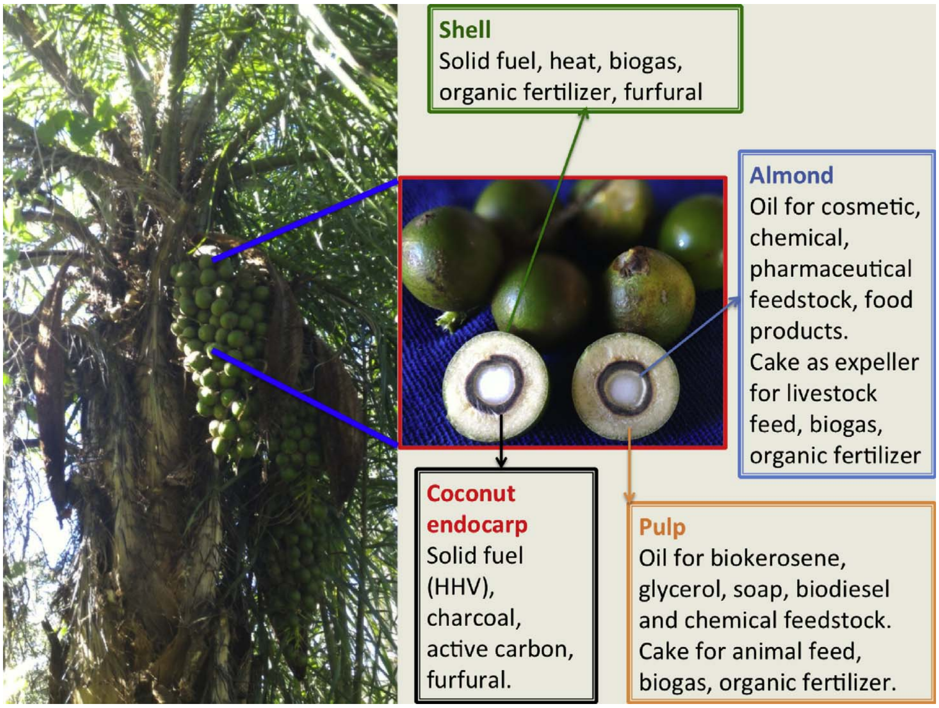

Fig. 1. Potential uses of Acrocomia fruit.

behavior while the hysteresis loop and its lignin contents exhibit a direct relationship [13]. New analysis has also found that a function of the elemental composition in mildly heat-treated wood can predict the occupancy of water sorption sites [14].

Though some char properties have been extensively studied [9,10], to our knowledge, no study concerning the evolution of elemental analysis, surface area and water vapor sorption properties during pyrolysis of coconut endocarp, exists.

The important role of biomass feedstock in the pyrolysis process is well known. The composition and physical properties of the pyrolysis products depends on the raw material properties. Holocellulose and lignin content in coconut endocarp, was determined by Evaristo et al. [1] and Reis et al. [2] and the intense lignification of its sclereids cells, provides its impermeability and petrous consistency [2,15].

In order to produce different fuels and chemicals from pyrolysis, the composition of raw material and thermal decomposition mechanism should be determined. Although there are extensive studies on the mechanisms of biomass pyrolysis [16–18], none is specific to this feedstock or the kinetic progress of its thermal decomposition.

In this study, mass loss as a function of time, in static conditions, were used to explain kinetic pyrolysis in the coconut endocarp. Three decomposition rates were observed from the mass loss vs time curves, related to the three main components' degradation. These measurements serves as the basis for future work in developing a kinetic model for biomasses of this type.

The major focus of this study is the experimental characterization of the coconut endocarp and its chars, obtained from a variety of isothermal pyrolysis conditions. It is important to propose the more relevant use of coconut endocarp and its chars, as *A. aculeata* is a potential feedstock for a biorefinery, likely to reduce deforestation and pollution.

The analysis techniques employed for this study included: elemental analysis, gas sorption analysis, water vapor sorption analysis, environmental and scanning electron microscopy (ESEM–FEG/SEM). In addition, the thermogravimetric TG and DTG curves, for the coconut endocarp and char samples were used as a tool for obtaining information about the main structural component's degradation. From our results, coconut endocarps could be used as feedstock to produce three different products: high-quality bio-oil or solid fuel (treatment at 250–300 °C), charcoal of different quality depending upon the end use (treatment at 350–450 °C), and feedstock to a gasification process (treatment above 500 °C).

2. Experimental

2.1. Materials and pyrolysis conditions

A. aculeata, indigenous to Paraguay, is usually found in areas situated between the latitudes 19 and 27 south and longitudes 54 and 62 west. The solid and woody residue inside the *A. aculeata* fruit, referred to as "coconut endocarp", was used in this study. The availability of the coconut endocarp, as agroindustrial waste in Paraguay, is about 7 tonnes of dry matter per hectare per year [19]. The feedstock was cleaned with water and dried in air flow at room temperature. Sample particles, between 0.2 and 0.63 mm selected from a previous work [7], were obtained using a grinder (IKA M20 Universal mill) and subsequently sieved.

The pyrolysis was carried out by a STA 449 F3 Jupiter, NETZSCH at atmospheric pressure. Each sample with an initial weigh of 10 ± 2 mg was placed in an alumina crucible and heated at 5 °C min^{-1} under a nitrogen flow of 50 mL min^{-1} (STP). Initially, samples were heated from ambient temperature to 100 °C, and dried for 30 min. The temperature was then increased to a final temperature (250, 300, 350, 400, 450, 500, 550 °C) and was observed, thereafter, for 2 h.

The percentage mass loss "*ml*" defined as the instantaneous anhydrous mass loss as a function of time, was calculated with the following equation (1):

$$\text{ml} = \frac{m_i - m_t}{m_i} \times 100 \tag{1}$$

where m_i is the anhydrous mass at the beginning of the thermal degradation (after they were dried at 100 °C for 30 min) and m_t is the anhydrous mass of the char residue (thermal treated sample) in the instant t of the thermal degradation. The final mass loss "*fml*" is measured at the end of the plateau for each selected temperature. This method was employed following previous testing in this lab which indicated that 30 min at 100 °C was enough time to release the moisture content in powder wood samples [20].