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Influence of Oxidative and Anaerobic Conditions on the Microstructure of the Cocoa Pod Husk Biochar for Environmental Remediation

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The valorization of agricultural residues through thermochemical conversion represents a promising strategy for environmental remediation and sustainable soil management. In this study, the influence of oxidative and anaerobic thermal conditions on the microstructure of biochar produced from cocoa pod husk (*Theobroma cacao* L.) was investigated. Biochars were obtained via slow thermal conversion using two systems: a laboratory-scale pyrolyzer and an electric muffle furnace, operated at 300 °C and 400 °C. Surface morphology and pore structure were characterized by scanning electron microscopy (SEM), while quantitative image analysis was performed using OpenCV-based processing to extract morphological parameters such as area, perimeter, aspect ratio, solidity, and equivalent diameter. Anaerobic pyrolysis at 400 °C promoted larger and more uniform porous structures; however, muffle-produced biochars also displayed morphologies suitable for environmental and agricultural applications, representing a viable alternative when access to dedicated pyrolysis systems is limited.

1. Introduction

During recent decades, the evident decline in petroleum reserves and the continuous demand for energy and raw materials have driven the scientific community to explore alternative and sustainable solutions across engineering, environmental, and agricultural sectors. In this context, soil revalorization and the mitigation of contaminants have gained increasing attention, particularly within frameworks promoting circular economy principles and the valorization of agricultural residues. Among emerging thermochemical strategies, pyrolysis has been widely applied to convert biomass residues into biochar for environmental applications. Cocoa pod husk (CPH) is a representative example of an abundant agricultural residue generated during cocoa cultivation and post-harvest processing (Maldonado-Mateus et al., 2025). This biomass is typically discarded without any added valorization, leading to the emission of CO_2 and other pollutants due to its natural decomposition in agricultural fields (Maldonado-Mateus et al., 2021). Recent studies have further highlighted CPH as a promising precursor for bioadsorbent production (Hernandez et al., 2024). The transformation of CPH into biochar therefore represents not only a waste management strategy but also an opportunity to generate value-added materials suitable for soil amendment and environmental remediation.

Significant advances in thermochemical technologies have been reported over the last decades, particularly regarding the design and operation of pyrolysis reactors. García-Núñez et al., (2017) present a comprehensive review of reactor configurations, including slow, intermediate, fast, and microwave-assisted pyrolysis systems, highlighting how variations in heating rate, residence time, and atmospheric control strongly influence biochar yield and physicochemical properties. Fluidized-bed, screw-type, and rotary drum reactors have demonstrated distinct operational advantages and limitations, depending on the feedstock and target application. However, this technological diversity also limits knowledge transfer and equipment scalability, especially in agricultural regions where access to specialized pyrolysis units remains restricted. Beyond feedstock availability, biochar production is often constrained by the need for robust and specialized equipment capable of maintaining

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controlled low-oxygen environments. Such systems are frequently expensive and technically demanding, which restricts their adoption by small-scale farmers and rural communities. In contrast, conventional muffle furnaces are more widely available in academic and local laboratory settings, yet their use for biochar production under oxidative conditions remains less explored, particularly in terms of how oxygen exposure affects biochar microstructure and functionality.

The performance of biochar in environmental and agricultural applications is governed not only by its bulk composition but also by its surface chemistry and pore architecture. Oxygen-containing functional groups (*e.g.,* hydroxyl, carboxyl, and carbonyl groups) play a critical role in cation exchange capacity, adsorption of contaminants, and nutrient retention and release mechanisms in soils (Hernandez et al., 2024). Similarly, pore size distribution and surface morphology influence water retention, microbial colonization, and mass transfer processes, which are essential for soil amendment and remediation efficiency. This study investigates how two thermochemical processing systems, namely a conventional muffle furnace (oxidative conditions) and a laboratory-scale pyrolyzer (oxygen-limited conditions), influence the microstructure of CPH biochar. Unlike previous studies primarily focused on pyrolysis-derived biochars, this work evaluates the feasibility of producing biochar under oxidative conditions using widely available laboratory equipment and combines SEM with OpenCV-based semiquantitative image analysis to compare pore morphology. This approach provides practical insight into decentralized biochar production for agricultural and environmental applications where dedicated pyrolysis systems are not readily available.

2. Materials and methodology

2.1 Raw material preparation

CPH biomass was collected from *Theobroma cacao* L. plantations located in Sarare region, Toledo municipality, Norte de Santander department, Colombia (7°36′29.14″ N, 72°37′45.23″ W; 961 m a.s.l.). After collection, the biomass was manually inspected to remove visible impurities such as soil particles and washed with distilled water. For the purposes of this study, the biomass was dried in a convection oven (Equip-Tech Ltda, Bucaramanga, Colombia) at 60 °C until constant mass was achieved, in order to reduce moisture content and minimize variability associated with water evaporation during subsequent thermal treatment. The total dry mass obtained was manually cut into pieces of *ca.,* 4 × 4 cm to ensure uniform heating during pyrolysis, and individual batches of 100 g were used for each pyrolysis experiment.

2.2 Biochar production under oxidative and anaerobic conditions

Biochars were produced by slow thermochemical conversion using two different systems: a laboratory-scale pyrolyzer (Design and manufacturing, University of Pamplona, Colombia), operating under oxygen-limited (anaerobic) conditions, and an electric muffle furnace (Neycrat Vulcan 3-550, Dentsply Neytech, USA) operating under atmospheric conditions (oxidative). For each experiment, 100 g of dried biomass was placed in the reactor and heated from room temperature (*ca.,* 20 °C) to the target temperatures of 300 or 400 °C at a heating rate of 10 ± 2 °C min^{-1}, followed by a residence time of 90 min. Temperature was continuously monitored using a K-type thermocouple positioned close to the sample holder.

The laboratory-scale pyrolyzer consisted of a sealed stainless-steel reactor designed to minimize oxygen ingress during thermal treatment and was operated without external gas injection, relying on the residual oxygen present inside the reactor. Conversely, the muffle furnace was operated under natural air atmosphere, exposing the biomass to oxidative conditions throughout the thermal treatment. All pyrolysis experiments were performed in triplicate to ensure reproducibility.

2.3 Morphological characterization by scanning electron microscopy (SEM)

The surface morphology and microstructural features of the biochars were analyzed using a scanning electron microscope (SEM, MIRA3 TESCAN). Biochars produced at 300 °C and 400 °C under both oxidative and anaerobic conditions were selected to evaluate the influence of pyrolysis atmosphere and temperature on pore development. Prior to analysis, the biochar samples were mechanically ground and sieved to a particle size of 60 mesh to obtain homogeneous particle fractions. The powders were mounted on aluminium stubs using conductive carbon tape and coated with a thin gold layer by sputtering to improve surface conductivity and prevent charging effects. SEM micrographs were acquired at an accelerating voltage of 30 kV and a magnification of 1000x, using secondary electron (SE) and backscattered electron (BSE) detectors, under high-vacuum conditions, to obtain complementary information on surface morphology.

The field of view was 166 µm, with a scale bar of 50 µm, allowing detailed observation of pore development and structural features of the biochars. Figure 1 shows the general scheme of obtaining biochar under oxidative and anaerobic conditions from the CPH of *Theobroma cacao* L.

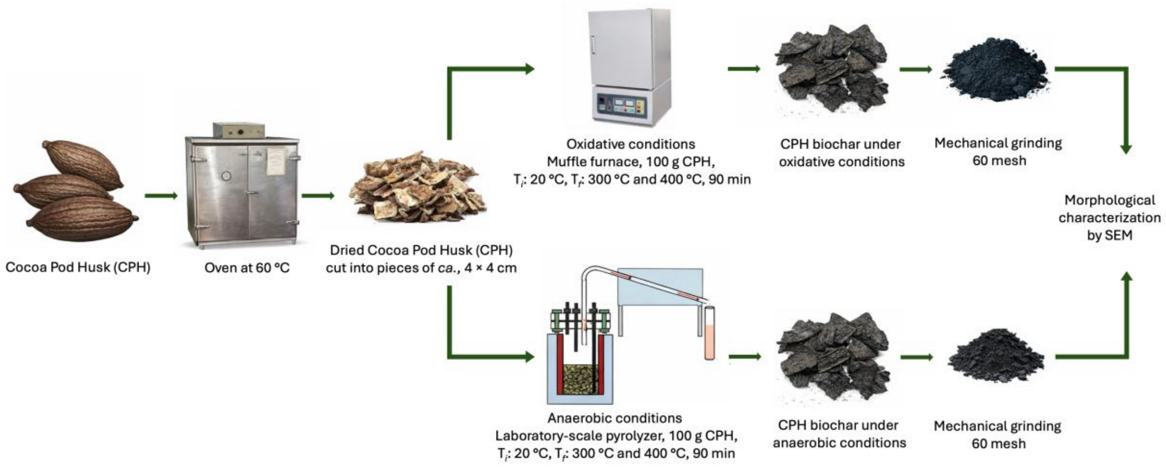

Figure 1: General scheme of obtaining biochars under oxidative and anaerobic conditions from the CPH of Theobroma cacao L.

2.4 Quantitative image-based porosity analysis

A total of sixteen SEM micrographs were acquired for the four experimental conditions (300 and 400 °C under anaerobic and oxidative atmospheres). Representative image fields were randomly selected from different regions of each sample to minimize local morphological bias. Quantitative image analysis was performed using OpenCV on the visible pore structures identified in each micrograph, and the reported values correspond to the mean ± standard deviation obtained from the analyzed pore population. The following morphometric parameters were calculated:

- Area (A), defined as the total number of pixels within the segmented pore region, was calculated using Eq 1.

$$A = N_p \cdot s^2 \quad (1)$$

Where:
N_p: number of pixels within the segmented object
s: Scale factor (µm per pixel)

- Perimeter (P) was calculated as Eq. 2.

$$P = \sum_{i=1}^{n} d_i \cdot s \quad (2)$$

Where:
d_i: distance between consecutive pixels of the contour

- Aspect ratio (AR) measures the elongation of the object and is defined as the ratio between the major and minor axes of the fitted ellipse. It was determined using Eq. 3.

$$AR = \frac{L_{major}}{L_{minor}} \quad (3)$$

Where:
L_{major}: length of the major axis
L_{minor}: length of the minor axis

- Extent (E) represents the ratio of the object area to the area of its bounding rectangle. It was calculated using Eq. 4.

$$E = \frac{A}{A_{box}} \quad (4)$$

Where:
A : area of the object
A_{box} : area of the minimum bounding rectangle

- Solidity (S) indicates the compactness of the object and is defined as the ratio of the object area to the area of its convex hull. It was calculated using Eq. 5.

$$S = \frac{A}{A_{convex}} \quad (5)$$

Where:

A_{convex}: convex hull area of the object

- Equivalent Diameter (D_{eq}) defines the diameter of a circle with the same area as the object. It was calculated using Eq. 6.

$$D_{eq} = 2\sqrt{\frac{A}{\pi}} \quad (6)$$

3. Results

Biochars produced under oxidative conditions (45.0 ± 0.5 %) exhibited lower yields compared to those obtained under anaerobic pyrolysis (55.0 ± 0.8 %), which can be attributed to partial oxidation and burn-off of the carbon matrix during thermal treatment in the presence of oxygen. Similar trends have been widely reported in biomass thermal conversion processes, where oxidative environments promote mass loss through CO and CO_2 formation (Crombie K., & Masek O., 2015).

3.1 SEM analysis of biochar morphology

To qualitatively assess the influence of temperature and processing atmosphere on biochar microstructure, SEM analysis was performed on samples produced at 300 °C and 400 °C under anaerobic and oxidative conditions, which is shown in Figure 2. At 300 °C, SEM micrographs revealed relatively dense and poorly developed porous structures for both production methods. At this temperature, thermal decomposition of hemicellulose and cellulose is still incomplete, and lignin-derived structures remain largely intact, resulting in a compact carbon matrix with limited pore opening, as reported in previous investigations on low-temperature biochars (Tu et al., 2022).

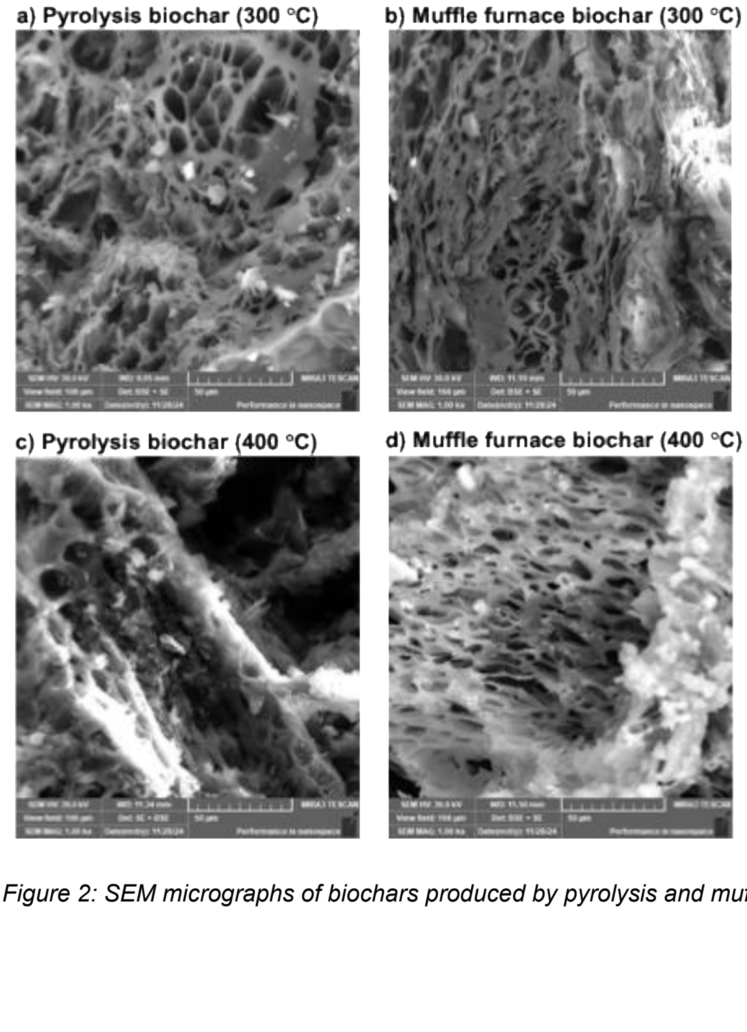

Figure 2: SEM micrographs of biochars produced by pyrolysis and muffle furnace at different temperatures.

At 400 °C, significant differences emerged between the two thermochemical processing systems, reflecting the combined effects of reactor configuration, heat transfer characteristics, and processing atmosphere on biochar development. Biochars produced by anaerobic pyrolysis exhibited a well-developed, interconnected porous network with relatively uniform pore distribution. This evolution is associated with enhanced devolatilization, progressive aromatization, and structural rearrangement of the carbon matrix, driven by the thermal cracking of biopolymers and release of volatile compounds (Keiluweit et al., 2010). This morphological evolution is consistent with previous studies indicating that higher pyrolysis temperatures enhance pore development due to the intensified thermal devolatilization of hemicellulose, cellulose, and lignin, which facilitates the release of volatile compounds and promotes the formation of internal porosity within the carbon matrix (Tu et al., 2022). At this temperature, pore expansion predominates over structural collapse, resulting in biochars with improved textural uniformity and accessibility. In addition, higher-temperature anaerobic pyrolysis promotes increased aromatic condensation and a relative depletion of oxygen-containing functional groups, yielding biochars with more hydrophobic surfaces and enhanced structural stability.

Conversely, biochars produced in the muffle furnace at 400 °C showed more heterogeneous and anisotropic pore structures. The presence of oxygen during thermal treatment induces partial oxidation of reactive carbon sites, leading to localized burn-off of pore walls and distortion of the original biomass-derived framework. Such oxidative effects have been described as partial gasification phenomena, which compromise pore integrity and structural uniformity (Gao et al., 2024). This oxidative environment also favors the formation of oxygenated surface functional groups, such as carboxyl, hydroxyl, and carbonyl moieties, which increase surface polarity and reactivity, enabling electrostatic interactions, hydrogen bonding, and cation exchange processes relevant to nutrient retention and metal immobilization in agricultural soils. To complement the qualitative SEM observations, image-based analysis was applied to quantify pore morphology parameters derived from SEM micrographs. This approach provides a semi-quantitative assessment of pore size, shape, and structural uniformity.

3.2 Quantitative image-based pore analysis

Table 1 summarizes the morphological parameters obtained from SEM image analysis of biochars produced at 300 °C and 400 °C under pyrolytic (anaerobic) and muffle furnace (oxidative) conditions. The parameters derived from OpenCV processing provide quantitative insight into pore size, shape, and surface uniformity.

Table 1: Quantitative morphological parameters derived from SEM image analysis of CPH biochars produced under anaerobic -pyrolysis- and oxidative -muffle- conditions.

Process temperature	300 °C		400 °C	
	Pyrolysis	Muffle	Pyrolysis	Muffle
Area, μm^2	213.5 ± 24.6	272.0 ± 37.8	269.0 ± 28.4	166.5 ± 25.1
Perimeter, μm	66.38 ± 6.21	80.53 ± 9.34	85.84 ± 7.12	61.80 ± 7.85
Aspect Ratio	0.9677 ± 0.082	0.6667 ± 0.091	0.9944 ± 0.075	1.6515 ± 0.18
Extent	0.5294 ± 0.038	0.5024 ± 0.046	0.5106 ± 0.034	0.5601 ± 0.052
Solidity	0.8818 ± 0.029	0.8196 ± 0.043	0.8701 ± 0.026	0.8999 ± 0.035
Equivalent Diameter, μm	16.49 ± 1.42	18.61 ± 1.93	18.51 ± 1.55	14.56 ± 1.73

At 300 °C, biochars produced in the muffle furnace exhibited higher area (272.0) and perimeter (80.53) values compared to those produced by pyrolysis (213.5 and 66.38, respectively), indicating the presence of larger but more irregular surface features. This observation is supported by the lower solidity (0.8196) and aspect ratio (0.6667) values, suggesting a more heterogeneous pore structure under oxidative conditions, consistent with incomplete carbonization (Sun et al., 2022). At 400 °C, anaerobic pyrolysis resulted in biochars with larger pore areas (269.0), higher perimeters (85.84), and aspect ratios close to unity (0.9944), reflecting more isotropic and interconnected pore networks. In contrast, oxidative biochars, samples produced in the muffle furnace at the same temperature, exhibited reduced area (166.5) and equivalent diameter (14.56), coupled with a markedly higher aspect ratio (1.6515), suggesting elongated and less uniformly distributed pores, likely due to enhanced oxidation and structural collapse. The extent parameter showed relatively minor variations across conditions, indicating that the overall pore occupancy within the bounding area remained comparable. However, variations in solidity reflect differences in pore wall integrity, with higher values at 400 °C pyrolysis (0.8701) and 400 °C muffle (0.8999) suggesting increased carbon framework consolidation at higher temperatures. From an application perspective, these structural characteristics suggest that while anaerobic pyrolysis produces biochars with superior microstructural uniformity, oxidative biochars obtained in a muffle furnace still retain pore structures that suggest potential suitability for applications such as soil amendment, where macroporosity, water retention, and microbial habitat are critical rather than high specific surface area. These observations are consistent with previous studies reporting the successful conversion of CPH into bioadsorbents for environmental applications (Hernandez et al., 2024). To further elucidate the mesoporous structure and surface area not fully captured by SEM-based analysis, future work will incorporate argon adsorption–desorption measurements, providing quantitative assessment of pore size distribution and textural properties relevant to environmental applications.

4. Conclusions

The results demonstrate that processing conditions, including reactor configuration, thermal environment, and processing atmosphere, significantly influence the morphological evolution of CPH biochar. Increasing the treatment temperature from 300 °C to 400 °C enhanced pore development, with the extent and uniformity of these changes dependent on the processing conditions. Although anaerobic pyrolysis produced biochars with more homogeneous pore structures, conventional muffle furnaces also generated biochars with morphological characteristics that support their potential use in agricultural and environmental applications.

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