

BIOCHAR FROM AMAZONIAN WASTE IN THE ESTERIFICATION OF PALM OIL DISTILLATE INTO BIODIESEL

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ABSTRACT

Valorizing solid waste is fundamental for the development of new sustainable products. In this work, Amazonian biochars were developed from murumuru husks and the alcoholic extraction residue of açai seeds for biodiesel production. The biomass was subjected to hydrothermal carbonization and functionalization with p-toluenesulfonic acid for the synthesis of biocatalysts. Biodiesel was obtained by esterification of the deodorized palm oil distillate. TGA and FT-IR analyses confirmed that PTSA functionalization was effective at 240 °C, highlighting S=O (1350 – 1040 cm⁻¹). The best biodiesel conversions with biocatalysts were 87.29% and 89.15%, with murumuru husk biochar at 2 hours and açai seed residue biochar at 4 hours, respectively. Thus, the bioproducts show potential in esterification reactions, as well as in stimulating biorefinery by utilizing three residual raw materials derived from murumuru (*Astrocaryum murumuru*), açai (*Euterpe oleracea*), and palm (*Elaeis guineensis*).

Keywords: Biochar. Murumuru bark. Açai seed residue. DDOP. Esterification. Biodiesel.

1 INTRODUCTION

In the search for sustainable, economical, and efficient products, biochar is an attractive alternative bioproduct for catalytic processes¹. Rich in green carbon, with high porosity and surface functionality, this material primarily comes from agricultural and processing residues, such as rice husk and sugarcane bagasse^{1,2}. The use of Amazonian residual biomass, such as murumuru bark and residue from the alcoholic extraction of açai seeds, contributes to the generation of value-added products. These raw materials are abundant in the northern region but are commonly improperly discarded into the environment³. This, therefore, provides an alternative destination, enabling the valorization of these organic solid wastes.

Palm oil deodorization distillate is one of the by-products generated by the palm oil refining process, lacking technological application or commercial value⁴. This residue contains high levels of free fatty acids, up to 84%, which allows its reuse in the esterification process to obtain biodiesel^{4,5}. Biodiesel is an alternative fuel to meet energy needs and reduce the environmental problems caused by petroleum-derived fuels⁶.

Therefore, this study aims to present the development of functionalized biochars with p-toluenesulfonic acid monohydrate, derived from murumuru shell and residue from alcoholic extraction of açai seeds, for biodiesel production using esterification of palm oil deodorization distillate.

2 MATERIAL & METHODS

The preparation of the biocatalysts and the catalytic tests followed the description by Laohapornchaiphan⁷. The biomasses used were murumuru shell and the residue from the alcoholic extraction of açai seeds. These biomasses were dried at 70 °C and sieved to 35 mesh to remove excess moisture and reduce particle size. The carbonization and functionalization process occurred in a stainless steel autoclave reactor using 9 g of biomass, with a mass ratio of 1:2 of p-toluenesulfonic acid monohydrate (PTSA), at 240 °C for 10 hours. The PTSA solution was prepared in a ratio of 3:10 (g.mL⁻¹). The biochars were ground, washed with heated distilled water, and dried at 110 °C for 24 hours.

The esterification of palm oil deodorization distillate (DDOP) was chosen as the catalytic test for obtaining biodiesel. The experiments were conducted using methanol, with a molar ratio of 1:60 of DDOP to methanol, using 5% biochar by weight of DDOP, at a temperature of 65 °C ± 5 °C for 2 hours or 4 hours. Afterward, the product was filtered and heated to 100 °C for methanol evaporation. Reactions were performed in duplicate. A control sample was prepared without the use of a catalyst. The conversion of DDOP to biodiesel was determined by titration of acidity, performed in duplicate, and calculated according to the following equation:

$$\% \text{ Conversion} = \frac{AV_o - AV_i}{AV_o} 100$$

where AV_o and AV_i represent the acidity values of DDOP before and after esterification, respectively.

The biomasses and biochars underwent thermogravimetric analysis (TGA/DTG), where samples were subjected to a temperature range from 25 to 900 °C, with a heating rate of 10 °C.min⁻¹ under a nitrogen inert atmosphere at 50 mL.min⁻¹, and Fourier-transform infrared spectroscopy with attenuated total reflection (FT- IR ATR), over a wavenumber range of 400-4000 cm⁻¹, with 64 scans and a resolution of 4 cm⁻¹.

3 RESULTS & DISCUSSION

The thermogravimetric analyses of the raw materials and functionalized biochars are depicted in Figure 1. In graphs A and B, the initial mass loss occurred between 25 and 150°C, attributed to the presence of moisture and volatile materials (VM) in the samples. Mass losses between 188 and 315 °C, 315 and 400 °C, and 400 and 900 °C correspond to the carbonization of hemicellulose, cellulose, and lignin, respectively, consistent with the structures present in lignocellulosic biomass as reported by Queiroz³. The mass percentage lost during the temperature increase of murumuru shell and açai seed residue is described in Table 01. In graphs C and D, a mass loss of PTSA in the biochar was observed between 110 and 240 °C, aligning with Laohapornchaiphan's⁷ findings. Thus, the hydrothermal process was successfully executed, potentially due to the removal of hemicellulose, allowing the carbonaceous materials to adhere to p-toluenesulfonic acid, thereby increasing porosity and enhancing reagent properties such as thermal stability and strong acidity.

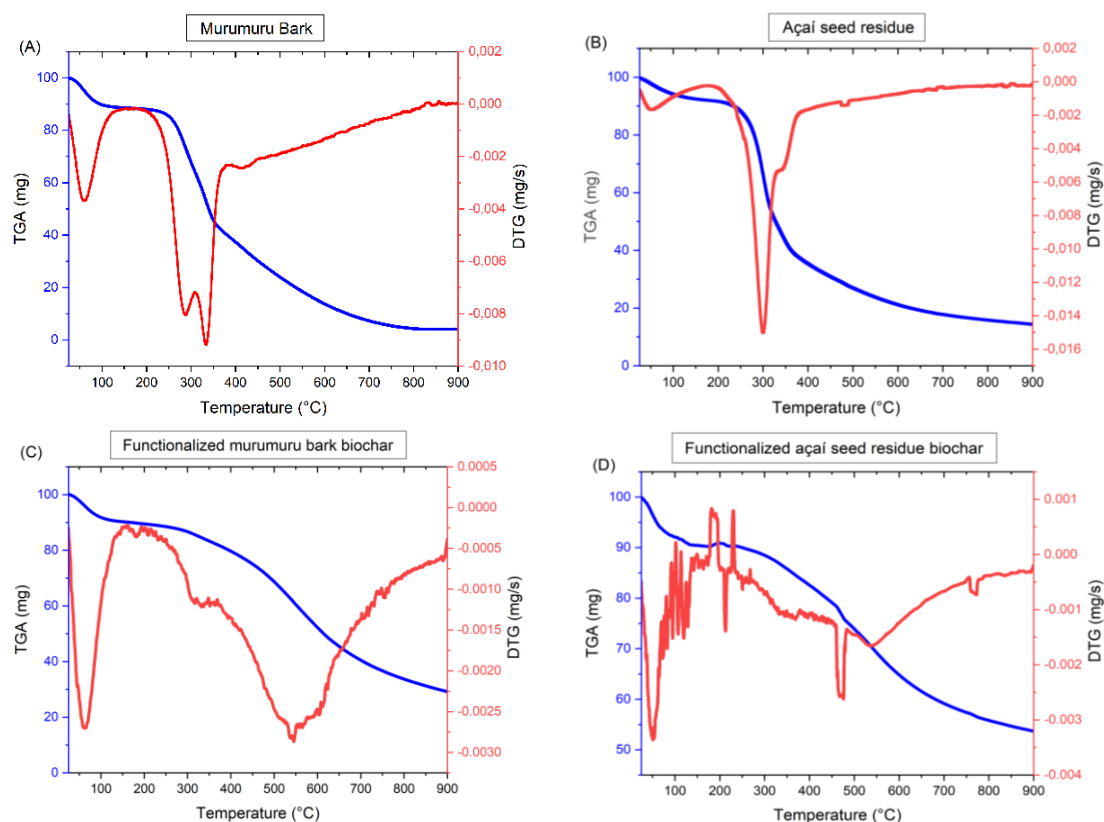


Figure 1 . TGA and DTG thermogravimetric curves: (A) Murumuru bark, (B) Açai seed residue, (C) Functionalized murumuru bark biochar and (D) Functionalized açai seed residue biochar.

Table 1 Mass loss in TGA of murumuru bark and açai seed residue.

Material	Temperature range (°C)	Mass loss of murumuru bark (%)	Mass loss of açai seed residue (%)
Water and VM	25 – 150	8	12
Hemicellulose	188 – 315	37	27
Cellulose	315 – 400	16	24
Lignin	400 - 900	25	33

FT-IR analysis allowed the identification of functional groups present in the samples. Figure 2 presents the results obtained for murumuru shell (MB), functionalized biochar from murumuru shell (FMBB), açai seed residue (ASR), and functionalized biochar from açai seed residue (FASRB). In the biocatalysts, bands of OH (3000-3700 cm⁻¹) indicating moisture, phenolic or carboxylic groups, C=C aromatic (~1573 and 1603 cm⁻¹), or NH₂ (1590–1550 cm⁻¹) characteristic of lignocellulosic biomass, C–O esters (1300–1020 cm⁻¹), and S=O (1350–1040 cm⁻¹) indicative of PTSA in the samples were detected, showing consistency with Laohapornchaiphan's⁷ findings.

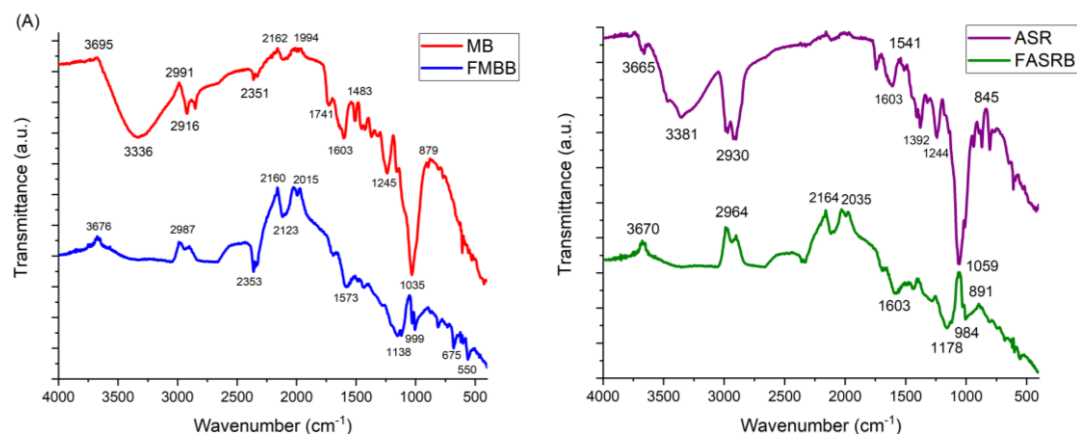


Figure 2 . FT-IR spectra (A) Murumuru bark and functionalized murumuru bark biochar, and (B) Açai seed residue and functionalized açai seed residue biochar

The results of the average conversion of DDOP into biodiesel using different Amazonian biocatalysts are described in Table 1. The functionalized murumuru biochar (BCM-PTSA2) showed the best performance in the 2 hours esterification, with a conversion rate of 87.29%. Due to the low conversion obtained with the functionalized biochar from açai seed residue (BCRA-PTSA2), a 4 hours experiment (BCRA-PTSA4) was conducted, resulting in a conversion rate of 89.15%, which represents a considerable improvement. These results highlight the potential of Amazonian biocatalysts in biodiesel production, especially compared to the process without a catalyst, which achieves only 10.52% conversion.

Table 1 . Average conversion of DDOP to biodiesel using amazonian biocatalysts, in duplicate.

Sample	% Average Conversion
Control	10,52
BCM-PTSA2	87,29
BCRA-PTSA2	56,81
BCRA-PTSA4	89,15

4 CONCLUSION

Biochars derived from residual biomasses demonstrated potential as amazonian bioproducts for use in biodiesel production through esterification using palm oil deodorization distillate. With TGA/DTG and FT-IR ATR, the effectiveness of carbonization at 240 °C via the hydrothermal process and functionalization with PTSA was observed, highlighting S=O ($1350\text{--}1040\text{ cm}^{-1}$). The best biodiesel conversions were achieved with the help of BCM-PTSA2 and BCRA-PTSA4, with average values of 87.29% and 89.15%, respectively. Furthermore, the production of these biocatalysts encouraged biorefinery utilization of three residual raw materials derived from murumuru (*Astrocaryum m.*), açai (*Euterpe o.*), and palm (*Elaeis g.*).

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