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Cocoa shell biochars for sustainable biodiesel production in Ecuador

Biocarbón de cáscara de cacao para la producción sostenible de biodiesel en Ecuador

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Abstract

The cocoa shells were ground to a #60 mesh size, then subjected to temperatures of 400°C and 600°C in a muffle furnace for two hours to produce a catalyst and biochar. Biochar was characterized using Scanning Electron Microscopy and Infrared Spectrophotometry. In the biodiesel production process, biochar served as an absorbent to filter impurities from the oil. The treated oil underwent transesterification in a double-jacketed reactor at 55°C for 120 minutes and 150 rpm. Biodiesel properties, including density, viscosity, and acidity index, were analyzed. Biochar's pore perimeter exhibited values of 15.23, 7.40, and 2.30 μm, indicating elongated blocks and dispersed pores with rounded and irregular edges. Significantly different results were obtained with p-values of 0.001 for viscosity, 0.013 for density, and 0.03 for the acidity index of biodiesel. A comparison between biodiesel processed with the biocatalyst and NaOH revealed differences in acidity index (0.19 vs. 0.30) and density (0.83 vs. 0.91 g/mL), respectively. The study demonstrates the effectiveness of biochar as a catalyst in enhancing biodiesel quality.
Keywords: Biocatalyst, sustainability, frying oil, valorization, characterization.

Resumen

Las cáscaras de cacao se molieron a un tamaño de malla #60 y luego se sometieron a temperaturas de 400°C y 600°C en un horno mufla durante dos horas para obtener un catalizador y biocarbón. El biocarbón se caracterizó mediante microscopía electrónica de barrido y espectrofotometría infrarroja. En el proceso de producción de biodiesel, el biocarbón se utilizó como absorbente para filtrar impurezas del aceite. El aceite tratado se sometió a transesterificación en un reactor de doble camisa a 55°C durante 120 minutos y 150 rpm. Se analizaron las propiedades del biodiesel, incluida la densidad, viscosidad e índice de acidez. El perímetro de poro del biocarbón mostró valores de 15.23, 7.40 y 2.30 μm, indicando bloques alargados y poros dispersos con bordes redondeados e irregulares. Se obtuvieron resultados significativamente diferentes con valores de p de 0.001 para viscosidad, 0.013 para densidad y 0.03 para el índice de acidez del biodiesel. Una comparación entre el biodiesel procesado con el biocatalizador y NaOH reveló diferencias en el índice de acidez (0.19 vs. 0.30) y la densidad (0.83 vs. 0.91 g/mL), respectivamente. *El estudio demuestra la efectividad del biocarbón como catalizador para mejorar la calidad del biodiesel.*
Palabras clave: Biocatalizador, sostenibilidad, aceite de fritura, valorización, caracterización.

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1 Introduction

Cocoa beans are mainly used for chocolate and cocoa-derivative food production, including cocoa paste, butter, powder and liquor. These products are largely consumed and appreciated around the world, showing a consumption growth rate in European Union and North America (1.7 and 3.6% annually, respectively). According to the last report of The International Cocoa Organization (2018), the cocoa beans production during the 2015/16 crop was estimated at 3.9 million tons. In parallel, it is estimated that 16 million tons of residual biomass were produced, taking in account based on the aforementioned dry weight of the fruit (80%) (Vazquez *et al*, 2019)

In the context of cocoa production (Figure 1) in Latin America, Ecuador holds a significant position, accounting for 7% of the world's production, ranking it third in terms of global cocoa production. Likewise, cocoa is one of the most traded goods around the world. México produced the first cocoa beans for more than two thousand years ago and it is one of the biggest cocoa beans producer and exporter in the world (Molina & Ramos, 2020). Cocoa is part of the cultural heritage in many areas of South and Central America and has played an important role in the history of human culture there. The modern methods of cocoa bean production for the purpose of the manufacture of modern chocolate are tied to the origin and development of cocoa bean fermentation and processing methods and the science of microbiology (Ozturk & Young, 2017)

To put this into perspective, in 2021, Ecuador exported approximately 350,000.00 tons of cocoa beans. Considering that cocoa beans constitute only 10% of the cocoa pod, this implies the production of 3,500,000.00 (three million five hundred thousand) tons of cocoa pods. Considering that cocoa husks make up 80% of the cocoa pod, it becomes evident that there are 2,835,000.00 tons of this biomass, originating from the cocoa crop, which are contributing to various environmental, agricultural, and health-related challenges as this residue decomposes on the farms.

The underutilization of waste, including its potential as a source of renewable energy, has been a driving force behind our research project. Our project focused on managing cocoa husk residues generated from cocoa cultivation in the El Oro province. The goal was to develop a biocatalyst to enhance the sustainability of biodiesel production from waste frying oils. Additionally, the biochar derived from this same residual polymeric matrix of cocoa husks was explored as a suitable material for application in circular economy processes. This approach aligns with the criteria of social, environmental, and economic sustainability, which are highly valued by our local farmers in Ecuador.

Figure 1. Cocoa pod.

Cocoa production not only brings about significant economic and social benefits but also results in the generation of substantial agricultural biomass waste. This waste includes cocoa shells and pruning leaves (Allegrini *et al*, 2022), which, in turn, leads to a considerable adverse environmental impact, characterized by the emission of various greenhouse gases and the leaching of contaminants that can significantly alter the nutritional composition of the soil and subsoil (Ayaz *et al*, 2021). Moreover, it contributes to the proliferation of pathogenic organisms, thereby increasing the spread of diseases (Cilas & Bastide, 2020). Global cocoa pod production was projected to reach 4.2 million tons in 2021. Approximately 85% of this production is made up of cocoa industrial waste, which includes bean shell (CBS), mucilage (CM), and cocoa pod husk (CPH). The cocoa business has both environmental and economic issues as a result of these wastes. By turning these byproducts into bioactive molecules, food ingredients, animal feed, biochemicals, biomaterials, and biofuels, the circular economy seeks to reduce waste (Mendoza *et al*, 2021).

In line with the United Nations' Sustainable Development Goals (2017) (ONU, 2017), particularly Goal 11, which focuses on creating sustainable and resilient communities and cities, the aim is to promote inclusivity and sustainability without imposing undue stress on natural resources and their functional attributes (CEPAL, 2017). On a different note, biodiesel is produced through a transesterification process where fats or oils react with a short chain alkyl alcohol in the presence of a catalyst (González *et al*, 2014). These biodiesel properties, including parameters such as density and viscosity, are also outlined in relevant standards.

To achieve efficient biodiesel production, it is essential to maintain precise control over reaction conditions and select an appropriate catalyst. In the transesterification process, the choice between homogeneous or heterogeneous catalysts depends on the characteristics of the feedstock (Maheshewari *et al*, 2022). Furthermore, the activation of the transesterification process can be achieved using either chemical or biological catalysts, both of which effectively facilitate the process (Ameen *et al*, 2022). While enzymes are the most commonly discussed biocatalysts, their utilization in commercial biodiesel processes is limited due to their relatively high costs and longer reaction times when compared to acid and alkali catalysis (Wang *et al*, 2023). With the current popularity of fried products, there is a growing issue surrounding the disposal of significant volumes of used vegetable oils, which poses challenges to both public health and the environment. A substantial amount of these oils is improperly disposed of, either directly into sewage systems or as regular household waste (Ravelo & Schallenberg, 2018).

One of the most prominent advantages of biodiesel is its non-flammable, non-explosive, renewable, and non-toxic biodegradable nature, resulting in minimal greenhouse gas emissions during combustion (Habibullah *et al*, 2015). Achieving this involves transesterification, a method recommended by the American Society for Testing and Materials (ASTM) due to its efficient oil conversion with the aid of a catalyst (Brahma *et al*, 2022). Moreover, biodiesel qualifies as a clean energy source (Mathew et al, 2021).

Transesterification relies on various parameters, including time, catalyst, speed, raw materials, and a crucial factor, temperature (Sánchez *et al*, 2020). An increase in temperature accelerates the reaction rate, facilitating both transesterification and saponification. When working with methanol, the boiling point ranges from 65°C to 70°C (Saavedra *et al*, 2019).

Other advantages of biodiesel include its absence of aromatic compounds, enhancement of the combustion process resulting in reduced CO emissions, improved lubricity when blended with fossil diesel, a nearly 50% reduction in CO emissions, a 78% decrease in CO2 emissions in its carbon life cycle, and it contributes to doubling the vehicle's lifespan due to its inherent characteristics (Atadashi *et al*, 2010).

Globally, biodiesel plays a significant role in various human activities, primarily in transportation, serving as energy for agricultural machinery and making substantial contributions to industrial development (Joshi *et al*, 2019).

2 Materials and methods

2.1 *Sampling of cocoa hulls*

Cocoa shells of the CCN51 variety were utilized in this study. The collected biomass underwent oven drying at a temperature of approximately 103 ± 2°C for a duration of 48 hours, following the ASTM E871 standard. Subsequently, it was appropriately packaged and labeled for subsequent analysis and experimentation.

2.2 *Cocoa Shell moisture*

Biomass moisture percentage was measured following the methodology suggested by official methods (AOAC, 2019), Moisture (Method 925.10).

2.3 *Preparation of biochar and catalyst*

The methods and procedures employed in this research are outlined as follows. The cocoa shells were initially processed in a mechanical mill to reduce their size and subsequently sifted through a 60-mesh screen. Next, they were loaded into porcelain crucibles for calcination, with temperatures set at 400°C and 600°C for two hours, yielding the raw materials required for catalyst and biochar production, respectively.

2.4 *Physical characterization of biochar by Scanning Electron Microscopy*

The biochar samples were not subjected to any pretreatment or coating. They were mounted in metal sample holders, using carbon conductive tape. A QUANTA FEG 650 field emission scanning electron microscope was used. The images were focused on the biochar particles in order to determine their microstructure.

2.5 *Chemical characterization of biochar by Fourier transforms infrared spectroscopy*

For the chemical characterization of the biocarbon obtained, an Agilent Cary 630 FTIR infrared spectrophotometer was used.

2.6 *Biodiesel production*

To conduct the biodiesel conversion tests using the waste frying oil, a preliminary treatment was applied. Initially, impurities, such as food particles from fried products, were filtered out, and excess moisture was removed from the waste oil, rendering it suitable as raw material for biodiesel conversion.

Table 1. Operating conditions to obtain biodiesel in the bioreactor.

TC	Biocatalyst Type	K_2CO_3
PC	Percentage of catalyst (m/m)	1,513
T°C	Temperature °C	55
R	Speed (rpm)	160
TP	Time (hours)	1

In the laboratory, the first step in the biodiesel preparation involved weighing two portions of 18.75 g each of the two biochars derived from cocoa shell calcination at 400°C and 600°C. These biochars were individually brought into contact with two portions of 300 mL of the preprocessed oil, creating two treatment groups to assess their impact on the ensuing biodiesel's characteristics.

The biochar serves as an absorbent for the micro-impurities present in the recycled frying oil. After the biochar absorbs the micro-impurities, it is separated from the oil through filtration using filter paper. Subsequently, the oil is placed in a double-jacketed reactor, where it is maintained at a temperature of 55°C and agitated at 150 rpm for 120 minutes to facilitate its transformation into biodiesel, aided by the cocoa shell catalyst.

The conditions for obtaining biodiesel are summarized in table 1.

Regarding the determination of the viscosity of the biodiesel obtained, the ball drop viscosity method cited by Camas, 2017 (Camas *et al*, 2017) was used.

2.7 Statistical analysis of results

To determine the statistical variance between the employed treatments (corresponding to different cocoa shell calcination temperatures and their effects on the physicochemical characteristics of biodiesel), a parametric Student's t-test for independent groups was applied. This was done after confirming that the data met the prerequisites of normality and homogeneity of variances. Normality was assessed using the Shapiro-Wilk test, and homogeneity of variances was verified using the Levene test.

3 Results

Biochar production, biochar yield and catalyst yield.

It was possible to obtain biochar from cocoa shells, as can be seen in Figure 9 above.

Physicochemical characteristics of biochar

Scanning electron microscopy was employed to analyze the biochar's morphology and the porosity of its mineral phases. Table 3 presents the descriptive analysis of the pore perimeter for cocoa biochar calcined at 600 °C, based on data obtained from three microscope images at magnifications of x870, x1000, and x15100.

At x8700 magnification, the average pore perimeter was 15.23 μm, with a maximum value of 20.39 μm. This is consistent with findings by Tomczyk *et al.*, 2020 (Tomczyk *et al*, 2020), who also reported values in the range of 5 to 20 μm at 500 °C, highlighting temperature as a significant factor in achieving well-defined pore edges. Pore perimeters at x1000 magnification varied from 5.01 to 9.78 μm, with an average of 7.4 μm. Prior studies have suggested that the pore perimeters of cocoa biochar may not be well-defined due to their occupation by carbonates and recalcitrant organic material.

Our findings align with the results for biochar microporosity at x15100 magnification, as the average pore perimeter measured was 2.30 μm. This change in pore size is attributed to the reduction of organic matter (Simón *et al*, 2022).

The cocoa pod biomass, rich in lignocellulose fibers, exhibits increased ash content when burned at temperatures exceeding 400 °C. Carbon content initially increases, but after 600 °C, carbon decreases, and the ash content rises. This leads to a more porous structure capable of absorbing chemical compounds. It's worth noting that biochar production involves three stages. The first stage (100 to 200 °C) uses heat to evaporate moisture and light volatiles. The second stage (200 to 500 °C) employs heat to break down cellulose, hemicelluloses, and other organic matter. In the final stage (> 600 °C), heat is applied to convert biomass into ash with high carbon content. The heat used at each stage significantly influences biochar properties, particularly its microporosity (Tomczyk *et al*, 2020).

The pore perimeters for cocoa shell biochar at different magnifications are summarized in Table 2.

Table 2. Micropore perimeter (μm) of biochar at three different magnifications: x870; x1000 and x15100.

Amplification μm	Median	SD	Min	Max
X 870	15,23	4,36	5,94	20,39
X 1000	7,40	2,23	5,01	9,78
X 15100	2,30	0,56	1,38	3,15

The scanning electron microscopy images taken at x 15,1k magnification (Figure 2) reveal two distinct geometric shapes. Firstly, elongated blocks indicative of a high specific surface area, and secondly, spring-like structures that disintegrate into ring-like formations. A porous structure on the specific surface is evident, along with scattered pores characterized by round and irregular edges. These observations are consistent with those made by Pinzon-Nuñez *et al.*, 2022 (Pinzon *et al*, 2022), who also noted similar microstructures in cocoa biochars. The image displays a series of pores forming tunnels with somewhat

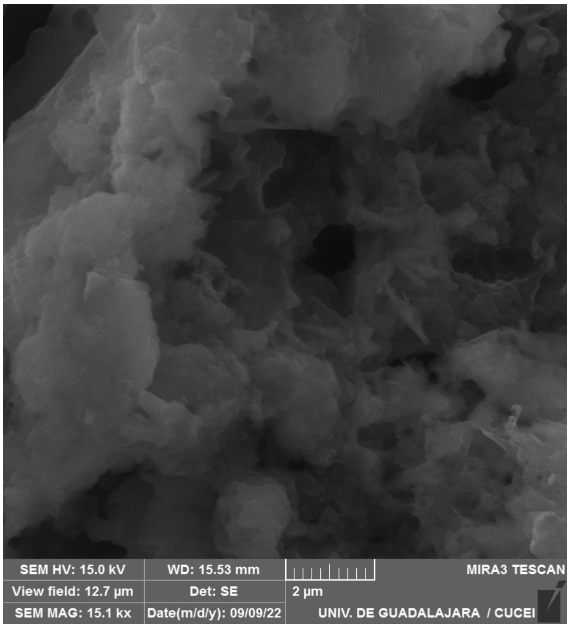

Fig. 2. Photomicrograph of cocoa biochar amplified x15100.

irregular edges, which extend into the biochar obtained in this study.

For the chemical characterization using FTIR spectroscopy, Figure 3 exhibits the infrared spectra within the 4000 to 500 cm^{-1} range (Figure 5 A) and within the 2000 to 1000 cm^{-1} range for both cocoa powder and cocoa shell biochar samples. It's noteworthy that both samples exhibit OH- (hydroxyl) groups within the 3800 to 3000 cm^{-1} range. A narrowing of the C-H and C=O bonds is observed between 2400 and 2350 cm^{-1} in the biochar obtained, while between 2000 and 1600 cm^{-1}, a peak for aromatic C=C bonds is present, indicating the presence of carboxylic acid in both samples. However, the transmittance is lower in the biochar, likely due to incineration at 600 °C (Folorunsho *et al*, 2022). A narrowing effect is evident in the biochar at 1400 cm^{-1}, indicating the presence of aromatic rings of C=O and C=C (Chen *et al*, 2022). The cocoa powder (not subjected to the calcination process) exhibits stretching at the 850 cm^{-1} band, suggesting the presence of carbonates, whereas the biochar sample at this wavelength band displays a more open vibration due to the high thermoconversion temperature (Bekele *et al*, 2022). This infrared profile is also consistent with observations made by Shin & Rowell, 2005, which suggests that when biomass rich in lignocellulosic fibers is subjected to very high temperatures, the release of oxygen and hydrogen occurs, leaving carbon atoms that form strong bonds with one another. The higher the temperature, the more carbon bonds are formed. Additionally, the reaction kinetics require a minimum speed of at least 600 rpm for effective mass transfer control in the triglycerides and methanol reaction (Bekele *et al*, 2022).

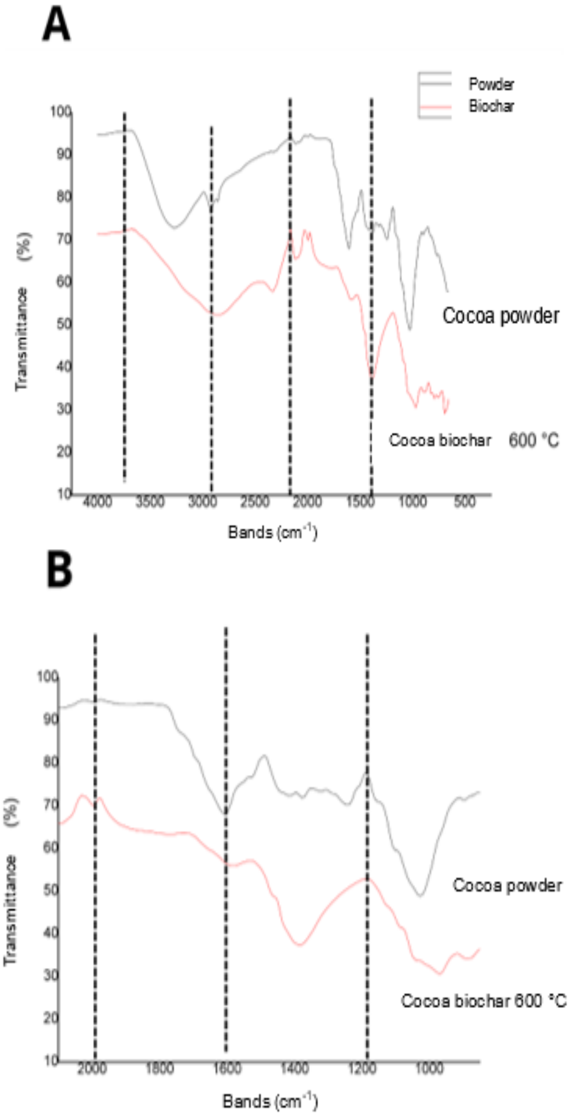

Fig. 3. Infrared spectra of cocoa powder sample (black line) and cocoa biochar at 600 °C (red line): x-axis is highlighted in A) bands between 4000 to 500 cm^{-1}; and in B) bands between 2000 to 1000 cm^{-1}.

Evaluation of the effect of cocoa shell biochar obtained at two temperatures on the physicochemical characteristics of biodiesel.

Two distinct biodiesel types (Figure 4) were derived from recycled frying oil, which had been pre-treated with the biochars obtained at 400 and 600 °C. These biochars were used in the pre-treatment process prior to transesterification with the previously mentioned catalyst. In this context, the influence of these two biochars on the physicochemical properties of the biodiesel was examined, encompassing parameters such as density, acidity index, and viscosity.

Furthermore, employing SPSS Statistics 25 software, it was possible to determine that there are highly significant distinctions in all statistical tests among the dependent variables. Specifically, a p-value of 0.001 was obtained for viscosity, a p-value of 0.013

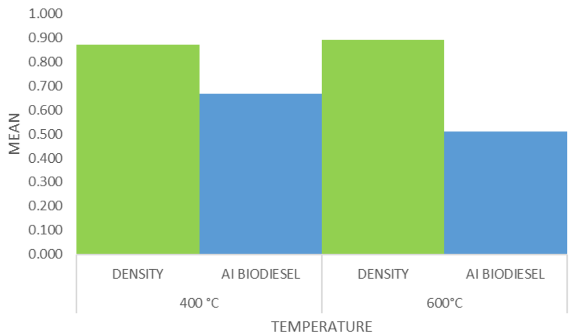

Figure 4. Comparison between density and acid number; as a function of biochars calcined at two temperatures (400 and 600 °C) used in this study during the pretreatment of recycled frying oil prior to its conversion into biodiesel.

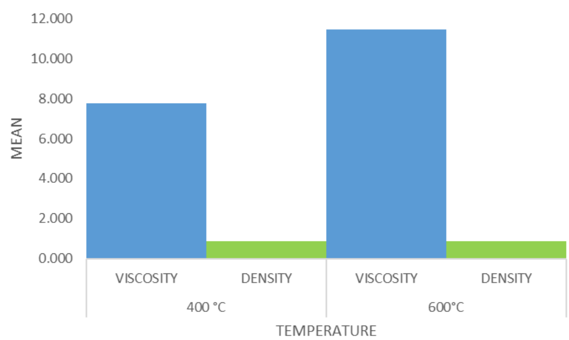

Figure 5. Comparison between density and viscosity of biodiesel as a function of calcined biochar at two temperatures (400 and 600 °C) used in this study during the pretreatment of recycled frying oil prior to its conversion into biodiesel.

for density, and a p-value of 0.03 for the acidity index of the biodiesel. These statistical parameters were evaluated for biochars calcined at temperatures of 400 and 600 °C. Furthermore, the data conform to the assumptions of normality and homogeneity of variances at a 95% confidence level.

3.1 *Effect of cocoa pod biochar catalyst on the organoleptic quality of biodiesel*

Regarding the effect of the catalyst on the organoleptic quality specifically the apparent color of the biodiesel obtained after transesterification.

3.2 *Physicochemical characterization of biodiesel*

In this sense, a value of 0.19 and 0.30 was obtained for the acidity of biodiesel with cocoa shell biocatalyst (K_2CO_3) and biodiesel with catalyst (NaOH), respectively. On the other hand, the densities for these products were 0.83 and 0.91 g/mL

Additionally, the humidity and viscosity of biodiesel obtained from biochar and cocoa shell catalyst were de 91,89 % and 3,67 poises.

Conclusion

Based on the experimental tests carried out in the present investigation, the following conclusions can be highlighted:

From this experimental investigation, several significant conclusions emerge. First, biochar derived from cocoa shells with a yield of 28.05% through a 400 °C calcination process was achieved. The potassium carbonate catalyst (K_2CO_3) obtained from cocoa shells yielded 6.05%, marking the beginning of research into its utilization for sustainable practices in cocoa cultivation and the transesterification of recycled frying oil into biodiesel.

Using the scanning electron microscopy technique, it was possible to establish the physical characteristics of the biochar obtained, specifically its morphology and the porosity of the mineral phases present in it. The descriptive analysis of the pore perimeter of the cocoa biochar calcined at 600 °C, allowed determining average values of 15.23, 7.40 and 2.30 um.

In this sense, considering that temperature is the main factor to obtain pores with well-defined edges (physical characteristic), our results ratify two geometric shapes in the crystalline microstructure of cocoa shell biochar. First, elongated blocks that indicate high specific surface area, which is an important factor when using this biochar to absorb impurities from recycled frying oil for its optimal and sustainable conversion into biodiesel, and also for its use in biosorption processes of environmental pollutants such as heavy metals in water and agricultural soil. Secondly, the scanning electron microscopies show a porous structure on the specific surface of the cocoa shell biochar, where scattered pores with round and irregular edges are also observed. On the other hand, the image captured at a magnification of x15100, shows a set of pores forming tunnels with not very regular edges.

Regarding the chemical characterization by infrared spectroscopy (FTIR), it was possible to determine the presence of OH- (hydroxyl) groups between the bands 3800 to 3000 cm^{-1}, while, at wavelengths between 2400 to 2350 cm^{-1} there is a narrowing of the C-H and C=O bonds in the biochar obtained at 400 °C. Likewise, it could be established that the cocoa powder (not subjected to calcination process) in the 850 cm^{-1} band there is a stretching, which indicates the presence of carbonates (carbon source due to the cellulose and hemicellulose present in this agricultural residue) in this wavelength band. Whereas, the biochar sample has a more open vibration due to the thermoconversion temperature, because, when biomass rich in lignocellulosic fibers is heated to very high temperatures, oxygen and hydrogen are released, leaving carbon atoms that form strong bonds with each other.

Using the SPSS Statistics 25 software, it was possible to determine by means of the p-value parameter (statistical significance) that in all the statistical tests there are highly significant differences between the dependent variables: p-value of 0.001 for viscosity, p-value of 0.013 for density, and a p-value of 0.03 for the biodiesel acidity index. These statistical parameters were evaluated for the biochars calcined at temperatures of 400 and 600 °C. Additionally, the data complied with the normality test and the homogeneity of variances at 95% reliability. It is concluded that the calcination temperatures of the cocoa husk used in the pretreatment process of the recycled frying oil do influence the physicochemical characteristics of the biodiesel obtained.

Additionally, the effect of the catalyst on the organoleptic quality, specifically the apparent color of the biodiesel obtained after transesterification, shows the clear difference in the color of two types of biodiesel obtained in this research work from the same recycled frying oil after 24 hours of resting in the separation funnel. In the biodiesel obtained by transesterification with the traditional method using sodium hydroxide and methanol (a method that generates chemical residues) an intense orange color can be observed, which is evidence of impurities, i.e. a lower quality, compared to the biodiesel obtained from the process of absorption of microimpurities with cocoa shell biochar and its subsequent transesterification using potassium carbonate (K_2CO_3) obtained from cocoa shells as a catalyst, which presented a light yellow color, evidencing a higher quality, which was ratified with the physicochemical quality parameters of both biofuels.

Ultimately, the biodiesel processed with the biocatalyst (K_2CO_3) displayed superior physicochemical properties, with an acidity index of 0.19 and density of 0.83 g/mL, compared to the biodiesel processed with the traditional catalyst (NaOH) with an acidity index of 0.30 and density of 0.91 g/mL. This underscores the higher quality of biodiesel produced using the proposed methodology.

The study's findings point to a number of possible applications and future opportunities. In addition to improving the quality of the biodiesel produced, potassium carbonate (K_2CO_3) and cocoa shell biochar can substitute conventional chemical catalysts, resulting in a decrease in the production of hazardous chemical waste. This approach can use agricultural wastes to produce biodiesel more sustainably and efficiently while also promoting a smaller environmental impact.

Furthermore, because of its high surface area and porous structure, cocoa shell biochar exhibits significant promise for the adsorption of pollutants in waterways and agricultural soils, helping to clean up contaminated areas. Biochar can improve soil structure and nutrient retention in agriculture, leading to more productive and sustainable farming practices. It is also possible to investigate the application of K_2CO_3 made from cocoa shells for other agricultural activities, like enhancing fertilizers and controlling pests with organic means.

Eventually, a more environmentally friendly and sustainable manufacturing cycle could be encouraged by the widespread use of these developed techniques and technology. Communities that are self-sufficient in energy might be established as a result, as well as supporting regional and global policies being put into place and technology and expertise being shared through seminars and training initiatives. Long-term industrial use of these methods can be facilitated by research on how to optimize the calcination process and their economic feasibility, which will greatly contribute to global sustainability and climate change mitigation.

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