

IN NATURA AND CARBONIZED COCONUT FIBER CHARACTERIZATION FROM PYROLYSIS PROCESS

CARACTERIZAÇÃO DE FIBRA DE COCO IN NATURA E CARACTERIZAÇÃO DO PROCESSO DE PIRÓLISE

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ABSTRACT

This work aims to verify the possibility of valuing coconut husk fiber through pyrolysis to produce carbonized and evaluate the influence of the pyrolysis conditions in its potential to use as a soil conditioner. Biomass were pyrolyzed used the peak temperatures of 350, 450 and 550 °C, with immersion time of 30 minutes. The characterization included analyses of bulk density, proximate analyses, X-RF, total carbon, pH, electrical conductivity, thermal analysis of biomass and cation exchange capacity in carbonized. The results indicate that the fiber has relevant properties for thermochemical conversion and the pyrolysis temperature influenced the characteristics of the carbonized. The X-RF showed that the carbonized presents K, Cl, Ca, Na and Mg content in its composition. The pH proved to be alkaline for the carbonized. It was possible to conclude that the carbonized produced have viable characteristics for its application as a soil conditioner.

KEYWORDS

Coconut fiber; Pyrolysis; Carbonized biomass; Biomass.

RESUMO

Este trabalho tem como objetivo verificar a possibilidade de valorização da fibra da casca de coco através da pirólise para produzir carbonizados e avaliar a influência das condições de pirólise no seu potencial de uso como condicionador de solo. A biomassa foi pirolisada utilizando as temperaturas de pico de 350, 450 e 550 °C, com tempo de imersão de 30 minutos. A caracterização incluiu análises de densidade aparente, análises proximais, X-RF, carbono total, pH, condutividade elétrica, análise térmica da biomassa e capacidade de troca catiônica em carbonizados. Os resultados indicam que a fibra possui propriedades relevantes para conversão termoquímica e a temperatura de pirólise influenciou nas características do carbonizado. O X-RF mostrou que o carbonizado apresenta teores de K, Cl, Ca, Na e Mg em sua composição. O pH mostrou-se alcalino para os carbonizados. Foi possível concluir que os carbonizados produzidos possuem características viáveis para sua aplicação como condicionador de solo.

PALAVRAS CHAVE

Fibra de coco; Pirólise; Biomassa carbonizada; Biomassa.



1. INTRODUCTION

Data from 2018 indicates that Brazil occupies the fourth position in the world ranking of coconut production with about 2.4 million tons, and a harvested area of 198.715 hectares (FAOSTAT, 2020). The growth of coconut tree cultivation in the country is due to its easy development in a tropical climate and the technologic advances in processing and conservation that make its commerce feasible. In contrast to its expansion in the country, the commercialization of coconut also generates potential adverse environmental impacts caused by its difficult disposal, of green coconut waste (Rosa *et al.*, 2002).

The traditional economic model tends to treat much of its solid waste only as tailings that follows a flow of production, consumption and disposal. The commercialization of green coconut in some places in Brazil still follows this route. According to the report from the Brazilian Agricultural Corporation of Research (Embrapa), of the amount of solid waste generated in Brazilian beaches, 70% are green coconut husks (GCH). According to Rosa *et al.* (2001), the lack of knowledge regarding the characteristics of the green coconut husk makes it so that this material is disposed of in a landfill as a waste, or just left in the open, when it can spread disease-causing vectors, becoming a public health issue. Correct processing of the components of the GCH post-consumption, such as the fiber coming from the fruit's mesocarp, is an alternative for this material to stop being treated as a waste and become a co-product. One of the options for the processing of the coconut fiber is its transformation in carbonized for agricultural purposes, like soil conditioner. This material is produced with the aim of application in the soil to improve its productivity, water filtration and Carbon storage (C). Guarnieri (2016) investigated the effects of carbonized material produced from coconut fruits added to sandy soil, and he concluded that the carbonized biomass favors aspects such as humidity conservation, nutrient retention (such as phosphorus and potassium), and an elevation of pH.

According to Lehmann and Joseph (2009), carbonized biomass is the carbon-rich product resultant from the pyrolysis process of organic materials such as wood, leaves, organic fibers, among others, which causes its thermal decomposition under limited conditions of oxygen and low temperatures (<700°C), different from charcoal produced for energy purposes. The availability of nutrients provided by the carbonized has a direct relationship with the type of biomass used, carbonization conditions, and soil in which it will be incorporated (Bibar, 2014). Slow heating rates and temperatures around 400 °C to 600 °C maximize the yield of solid coal, thus characterizing the slow pyrolysis, which is divided into carbonization and conventional pyrolysis, since carbonization focuses on the production of charcoal (Basu, 2010; Luengo; Felfli; Bezzon, 2008).

On pyrolysis and its influences in the characteristics of

carbonized, that the higher the peak temperature, the higher the results of pH, C, ash content (Souza *et al.*, 2021), C stability, and aromaticity in the carbonized biomass (Novotny *et al.*, 2015). Conz (2015) adds that the minimum temperature for the production is 360 °C, since from that temperature the resistance to biological and thermal degradation is higher. Major *et al.* (2009), on the other hand, state that pyrolysis temperatures above 500 °C favor the increase of the porosity and surface area of the material, which helps in the sorption of nutrients. Still, apart from the peak temperature, other meaningful variables for the pyrolysis, as Schena (2015) points out, are the inert gas flow, if there is any, and heating rate in the oven.

According to Hou (2021), biochar can promote more sustainable soil management and even contribute to achieving the United Nations' Sustainable Development Goals (SDGs). The physical and chemical properties of the carbonized biomass, as well as the pyrolysis temperature, are directly related to the operating conditions for its processing (Tomczyk *et al.*, 2020), and these same properties influence the way this material affects the soil. Therefore, the present article aims to evaluate the influence of carbonization temperature in the final properties of the carbonized material, pursuing its potential use as a soil conditioner.

2. MATERIAL AND METHODS

In this item, the characterization techniques of the coconut fiber *in natura* and the acquired biochar are shown, as well as details of the thermochemical process and its operational parameters.

2.1 Chemical and physical characterization of coconut fiber in natura

The coconut fiber used for the research comes from the green dwarf type coconut, acquired from the Rio Grande do Sul Supply Center-CEASA, located in the city of Porto Alegre. Originally, 17 coconuts were processed for the project, but there is no estimate of how many were used entirely to carry out the methodology. The processing for extraction of the fiber was carried out through manual removal of the coconut water and copra, and defibration in a mechanical equipment.

The characterization of coconut fiber in natura included analyses of real bulk density (BD), semi-quantitative X-ray fluorescence (X-RF), total Carbon (TC), proximate analyses (moisture, ash, volatile materials and fixed Carbon content), pH, conductivity (EC), higher calorific value (HCV), thermogravimetric and derivative thermogravimetry analysis (TGA/DTG), and differential thermal analysis (DTA). The standards used for the chemical and physical characterization are presented in Table 1. For the pH and EC analyses, it was necessary to perform the preparation of the samples, which had the methodology of passing the total of the sample as received through a 19 x 19 mm mesh sieve.

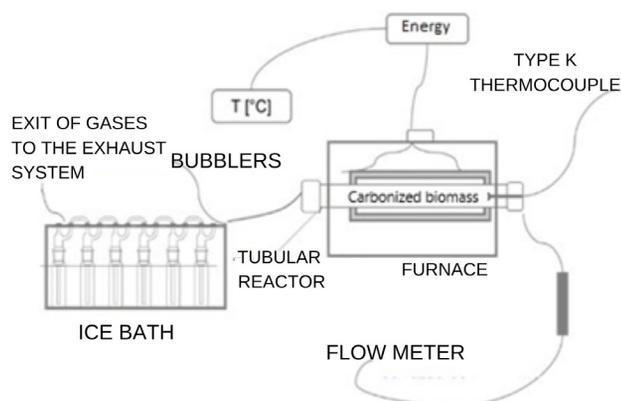


Figure 1: Schematic of the oven and gas cooling process.
 Source: Souza, 2019.

2.2 Thermochemical process and obtaining of the carbonized

The pyrolysis was carried out with a heating rate under N₂ inert atmosphere with a fixed flow (L/min) in a muffle oven (Sanchis model) with a quartz horizontal tubular reactor with a maximum temperature capacity of 1200 °C. For the collecting of volatiles during the pyrolysis, a cooling system, or condenser, was connected to the manual valve of the reactor outlet, adapted from Manera *et al.* (2018).

The collecting system consisted of 4 glass bubblers, which were filled with approximately 5g of cotton with the purpose of filtering and condensing the bio-oil generated. The non-condensable vapors went to a hood where they were filtered before atmospheric release. Figure 1 shows the schematic of the pyrolysis with the condensate collecting system.

The operating conditions for the performance of pyrolysis were peak temperature of 350 °C, 450 °C and 550 °C, with immersion time of 30 minutes at the defined temperatures, the approximate heating rate at 10 °C/min, and Nitrogen flow of 0.2 L/min. For each pyrolysis, it was used around 46g of fiber deposited in 410 stainless steel crucibles, and the experiments were carried out in duplicate for each defined condition. The samples of coconut fiber in the steel crucible before (a) and after (b) the pyrolysis are shown in Figure 2. The pyrolysis process occurred with the coconut fiber in natura on a wet basis. The post-pyrolysis procedure consisted of waiting for the oven to reach room temperature (25 °C) to remove the material from the reactor. Each sample was weighed before and after the thermochemical process, in which to determine the yield of the material, the initial mass of the biomass was transformed in a dry base through subtracting the moisture content obtained by the immediate analysis of the fiber in natura.

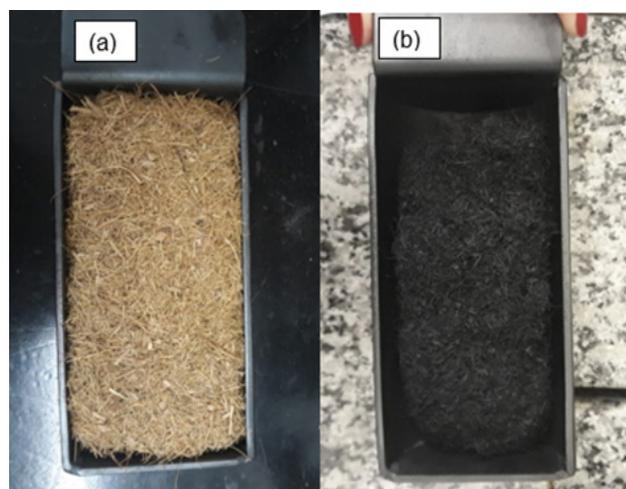


Figure 2: Coconut fiber in natura (a) and coconut fiber carbonized post pyrolysis (b).
 Source: Author, 2022.

The yield was determined through the equation (Equation 1) from Protásio *et al.* (2014), where the resultant mass (g) of carbonized is divided by the initial mass (g) of the biomass in a dry base:

Equation (1)

$$\text{Yield (\%)} = \left(\frac{\text{mass of carbonized}}{\text{mass of biomass}} \right) \times 100\%$$

2.3 Physical and chemical characterization of the carbonized coconut fibers

For the characterization of carbonized coconut fiber, analyses were carried out of real bulk density, semi-quantitative X-RF, total Carbon, Immediate Analysis, pH and electrical conductivity, whose methodologies were the same used for the characterization of the chemical and physical properties of the coconut fiber in natura. Cation exchange capacity (CEC) analyses were also executed.

The CEC analysis was performed in the Soil Analyses Laboratory of the Federal University of Rio Grande do Sul - UFRGS. The methodology applied followed the Normative Instruction - MAPA n° 28, (BRAZIL, 2007). The samples were dried and macerated in an Agate Graal to be of adequate granulometry (<0.5 mm), and dried at 65 °C in an oven for approximately 8 hours before the analysis, in which approximately 5 g of material of each sample was used.

3. RESULTS AND DISCUSSION

The results of the characterization performed before and after the thermochemical process of the biomass and the analysis of the influence of the temperature in the results are shown in the following sub-items, as well as the final evaluation of the valorization of the carbonized material as soil conditioner.

3.1 Relation of the properties of biomass in natura and carbonized biochar

Table 1 shows a synthesis of the comparative results between coconut fiber in natura and carbonized at 350 °C (B350 °C), 450 °C (B450 °C) and 550 °C (B550°C) with immersion time of 30 minutes in each temperature.

In the immediate analysis, the fiber moisture was of 6.75%, lower than the values found, also for coconut fiber, by authors such as Ferreira *et al.* (2016) (12.8% w.t.) and Esteves, Abud and Barcelos (2015) (13% w.t.). Although the analysis conditions and the origin of the fibers are not similar, there is a tendency for the moisture of this material to be reduced after processing. The moisture of the carbonized, in comparison with the coconut fiber in natura, decreased its content, consequence of the characteristic dehydration of the combustion stages. However, it was observed a small decrease between biomass and post-pyrolysis, which can be a result of the storage conditions of the material.

There was an increase in the ash content, in comparison with the in natura fiber. According to Padilla *et al.* (2018), this behavior can be explained by the removal of volatile materials because of the pyrolysis, increasing the fraction of mineral elements between the constituents of the carbonized. The ash content may be related to the presence of mineral substances, such as silica, aluminum, iron and calcium, and, in lesser quantities, of magnesium, titanium, sodium and potassium. (Basu, 2010).

The behavior of the volatile material content in the samples was decreasing with the increase of the pyrolysis

temperature, and a great variation in relation to the fiber, as it concerns the mass of the original material that is lost during the pyrolysis. In the immediate analysis of the fiber in natura, the content of VM and FC were proved to be majority (78.20% and 18.42%, respectively), indicating a high constitution of organic substances, a typical value for agricultural waste biomasses (Agrizzi, 2017). On the other hand, in the carbonized samples, with the increase of the temperature, there was a decrease of the VM, and an increase in the FC content, reaching 75.96% in the B550 °C sample.

According to Downie, Crosky and Munroe (2009), the increase in temperature, loss of volatiles, and the consequent restructuring of the crystallinity of the samples lead to the increase of the real bulk density in comparison with its raw materials, which can be seen in Table 1 in relation to the BD.

The release of condensable gases, non-condensable gases and water has consequently the increase of the concentration of C. Thus, VM content of the carbonized coconut fiber is inversely proportional to the FC, which is evidenced in the present analysis (MAIA; LIMA; GUIOTOKU, 2013). This behavior is also seen in the TC content, when contemplating organic and inorganic C, when it reaches 22.79% in the in natura sample, and in the post-pyrolysis it was between 65.95% (B350 °C) and 77.09% (B550 °C).

Regarding the pH found, the fiber, still as biomass, shows an acidic character of 4.55. In the literature, the values found for the pH of the coconut fiber are also low and vary from 4.2 to 5.9 (CABRAL, 2015; SILVA *et al.*, 2013;

| Parameter | Method | Units | Biomass in natura | B350 °C | B450 °C | B550 °C |
|--------------------------------|--|--------------------|-------------------|---------|---------|---------|
| Moisture content | CEN/TS 14774-1:2004 | % | 6.75 | 5.06 | 4.64 | 4.06 |
| Volatile Material content (VM) | CEN/TS 15148:2005 | % | 78.2 | 32.33 | 24.43 | 15.53 |
| Ash content | CEN/TS 14775:2004 | % | 3.38 | 8.41 | 11.48 | 10.5 |
| Fixed Carbon content (FC) | ABNT NBR 8112 | % | 18.42 | 59.26 | 64.09 | 75.96 |
| TC | Carbon and Sulfur Analyzer | % | 22.79 | 65.95 | 72.76 | 77.09 |
| BD | Pycnometer (gas Helium) | g.cm ⁻³ | 1.26 | 1.30 | 1.38 | 1.44 |
| pH | Normative Instruction n° 17 (MAPA, 2007) | | 4.55 | 7.85 | 9.38 | 9.56 |
| EC | Normative Instruction n° 17 (MAPA, 2007) | µS/cm | 1280 | 1260 | 1580 | 2280 |
| CEC | Normative Instruction n° 28 (MAPA, 2007) | mmol/kg | - | 81 | 71 | 17 |

Table 1: Physical-chemical characterization of the fiber in natura and carbonized.
Source: Author, 2022.

SILVEIRA, 2018). The data from Table 1 show an increase in the alkalinity of the carbonized as the temperature increases, which has an almost neutral characteristic in B350 °C, and reaches the maximum registered in B550 °C, when it reaches 9.56.

While the pH from the biomass to the carbonized had a marked change, going from acid to basic after the thermochemical conversion, the same did not occur in relation to the EC, in which the value of the in natura fiber showed itself even higher than the values of the carbonized sample at 350 °C, and that was only overcome with the increase from the sample at 450 °C.

The CEC analyses do not show a comparison with the biomass, as it was performed only in the carbonized material. Its results were contrary to the previous ones (pH and EC), for showing values that decrease as the pyrolysis temperature increases. The influence of such a factor will be discussed in the next sub-item. However, the CEC values may be related as well with the chemical composition of the samples, in which there was a higher value of CEC in the sample with the higher Potassium (K) and Calcium (Ca) content. Figure 3 shows the chemical composition, performed through semi-quantitative X-RF analysis, for the fiber and carbonized samples.

The sample of coconut fiber in natura showed more expressive contents of K (2.06%), Ca (0.59%) and Cl (0.51%). The fiber has its components strongly influenced by its origin, planting/harvesting season, location and management of cultivation apart from climate conditions, which can cause the variations in chemical composition; elements such as K, Ca and P are commonly found in the elemental matrix of the coconut fiber referring mostly to the cultivation and fertilization (ROSA *et al.*, 2001).

In relation to the chlorine content (Cl) found in the biomass, authors attribute it to the salinity of the fiber. According to Carrijo, Liz and Makishima (2002), the coconut husk can show high levels of tannin, potassium

chlorides and sodium, whereas Ito *et al.* (2010) brings attention to the fact that the Cl is a micronutrient found in many fertilizers used in the fertigation of crops such as the green coconut, which can be absorbed by it.

When compared to the chemical analysis of the carbonized, a variation in the content of most elements was observed. In addition to the TC, there are still significant values in the carbonized in terms of K, Cl, Ca (which were detected only in the B350 °C sample), followed by Sodium (Na) and Magnesium (Mg). These results were also observed by Paz (2017) and Suman and Gautam (2017), who, when analyzing carbonized of coconut fiber, noticed a large portion reserved to carbon, followed by smaller but relevant portions, due to the proportion of K, Cl, Ca and Na, except for differences related to the pyrolysis method and origin of the biomasses.

According to Bibar (2016), the fraction of nutrients in the carbonized is related to the fraction of ash, thus, it was expected that the highest ash content corresponds to a better distribution of nutrients in the samples.

3.2 Influence of the temperatures of 350 °C, 450 °C and 550 °C during the thermochemical process in the final properties of the carbonized

The pyrolysis process covers different phases of decomposition and the cellulose, hemicellulose and lignin contents influence in the yield and chemical and physical characteristics of its derivatives. Therefore, before the thermochemical process, the thermal analysis and calorific value analysis of the GCH fiber were carried out.

Figure 4 presents the thermogravimetric (TGA) and derivative thermogravimetry analysis (DTG), showing the thermal behavior of the degradation of the material in natura.

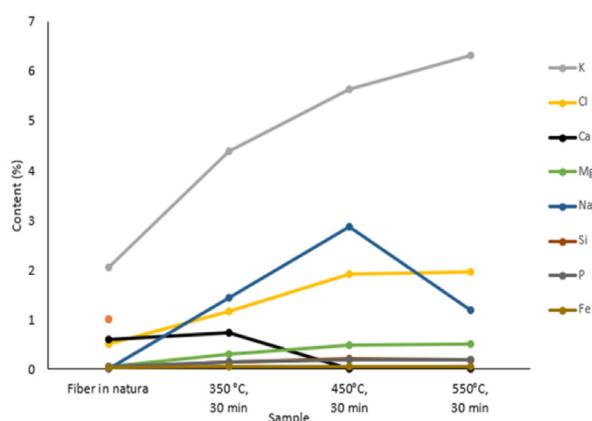


Figure 3: Chemical analysis of the fiber *in natura* and carbonized.
 Source: Author, 2022.

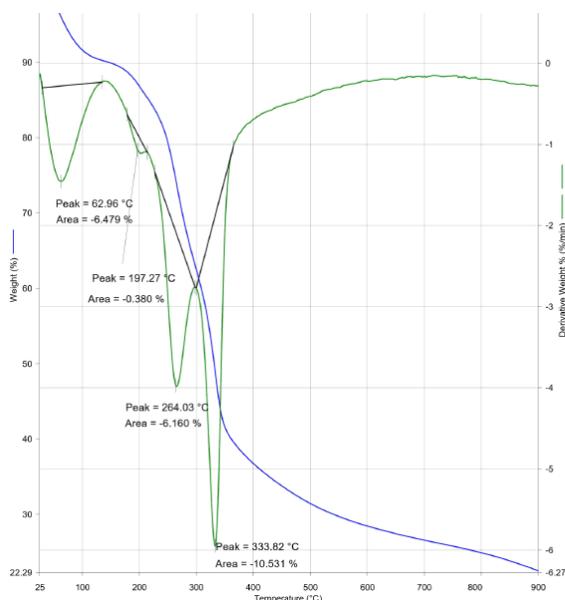


Figure 4: TGA/DTG of the sample of coconut fiber *in natura*.
 Source: Author, 2022.

In Figure 4, four peaks of mass loss of the sample studied can be noted. The first event observed in the degradation curve of the coconut fiber in natura is in the range between 25° C and approximately 150° C (TpeakDTG=62.96°C), referring to the removal of humidity in the sample. In this range there was a dehydration of 9.34%, which compared to the moisture value shown in the immediate analysis of the fiber (6.75%), is higher. According to Andrade and Carvalho (1998), close to this range at 150 °C, the beginning of the degradation of the lignin can also occur, which decomposes slowly and in continuity with the other compounds up to temperatures above 500 °C.

The second stage, between 180 °C and 220 °C (TpeakDTG=197.27°C), is associated to the decomposition of products, which happens in the range of 100 to 250 °C in biomass samples (Almeida, 2008).

The third peak is related with the presence of hemicellulose, occurring between approximately 235 °C, up to 297 °C (264.03°C), followed by the curve of decomposition of the cellulose, between 300 °C and 365 °C (TpeakDTG=333.82°C).

In Figure 5, the enthalpy variations suffered during the thermal analysis of the coconut fiber are shown during the DTA analysis.

The DTA curve shows that the biomass degradation reactions involve, initially, an endothermic reaction (25-110 °C), followed by 4 exothermic peaks (120-195 °C, 230-310 °C, 320-375 °C and 385-440 °C). In comparison with the TGA curves, the enthalpy analysis of the reaction shows that the first endothermic peak and a part of the first exothermic peak are within the range considered for the dehydration period of the sample and degradation of

products.

In DTA, the exothermic peaks are in a temperature range, in which the TGA shows the predominance of the degradation of organic matter, related to hemicellulose and cellulose, with its temperature range of degradation related to the second and third exothermic peaks. The last exothermic peak may still be related with the completion of the lignin decomposition, since its degradation still happens around 440 °C.

For the biomass pyrolysis, the TGA/DTA indicated that the chosen temperatures for the work (350°C, 450°C and 550°C) are inside of a range in which the thermal conversion of most compounds is complete, however, maintaining a considerable mass loss to obtain the resulting solid fraction, which is the carbonized.

In relation to the higher calorific value of the coconut fiber, the value found was of 18.91 MJ/kg, considered a value consistent with the other authors who analyzed the same type of biomass, such as Padilla *et al.* (2018), who found 18.67 MJ/kg, and Silveira (2018), with 17.46 MJ/kg. The coconut fiber observed also possesses a value considered high when compared with the rice husk analyzed by Vieira (2018) with 15.77 MJ/kg and Schropfer (2018) 14.055 MJ/kg, showing that the coconut fiber has an attractive calorific value as a biomass in an energy conversion situation.

Figure 6 shows the average values compiled from the yield of the solid fraction of the post pyrolysis biochar for each sample. Only the moisture content of the fiber was discounted from the yield values to obtain values in a dry base, the ash content was not discounted, as it was intended to demonstrate the yield of each carbonized in its entirety.

When analyzing the parameters that underwent variation throughout the process, it is noted that from 350 °C to 550 °C the average yield decreases. The pyrolysis temperature is relevant, as it is involved with the fundamental physical changes, such as, for example, the release of volatiles. In the TGA analysis of the fiber, a higher mass loss

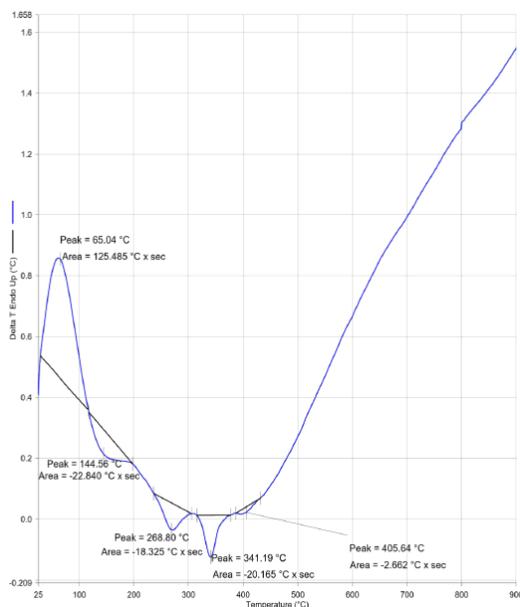


Figure 5: DTA of the sample of coconut fiber in natura.
Source: Author, 2022.

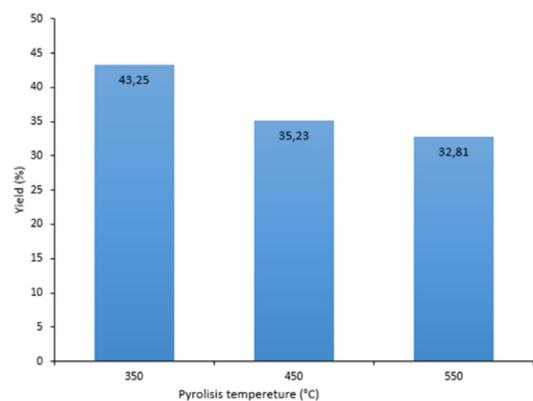


Figure 6: Average yield of the carbonized samples in dry base.
Source: Author, 2022.

was already evident from the degradation of the organic matter at around 180 °C, and the cellulose degrading between 365 °C, still having an influence from the slow degradation of the lignin, up to 450 °C. This shows that the yield tends to decrease according to the increase of temperature and degradation of these compounds.

According to Maia, Lima and Guiotoku (2013), from 450 °C the difference in conversion becomes milder, since the lignin is close to its maximum of thermal decomposition, thus, from approximately 500 °C in the TGA, the sample loses mass more slowly, which explains the proximity between the yield values of the samples at 450 °C and 550 °C.

The pyrolysis temperature also influenced in the results of the immediate analysis, in which there was removal of humidity from the sample as the temperature increased, and as already mentioned, its low decrease rate, from 350 °C (5.06%) to 550 °C (4.06%), either due to the retention of humidity acquired by the material in the interval between the performance of the pyrolysis and the analysis.

In the ashes there was a varied behavior, in which the ash content had an increase from 350 °C to 450 °C, however, it decreased again in the carbonized sample at 550 °C. The ashes tend to increase with the increase of the pyrolysis temperature, due to the loss of organic material, however, certain elements, such as P, K and S, tend to volatilize at temperatures around 500 °C, therefore it is possible that the ash contents are underestimated from such a temperature (MAIA; LIMA; GUIOTOKU, 2013; ENDERS *et al.*, 2012).

The levels of VM had a decrease between the analyses from 350 °C to 550 °C. On the other hand, the FC had an increase between that same interval. According to Sohi *et al.* (2010), the pyrolysis at lower temperatures may be adequate to have a control of the release of fertilizing nutrients, while higher temperatures would result in a material comparable to activated carbon.

Regarding the chemical analysis of the samples, there was a behavior of decreasing the content in relation to the increase of the peak temperature, as mentioned before, however, the behavior of some specific elements stands out, such as the total S, when there was an increase of the content with the high temperature. Zhao *et al.* (2018) described similar behavior in waste from cotton crops pyrolyzed at different temperatures, attributing the fact to the presence of volatile compounds with a low S content, and/or organic compounds resistant to temperature cracks and formation of mineral sulfates in their sulfur bonds.

Cl, Ca and P had their content reduced after the carbonization of the samples. This behavior is connected to its volatilization. In the case of Na, it increased when compared to the in natura biomass in peak conditions at 450 °C,

decreasing again in the sample at 550 °C.

In relation to K, there was an unusual behavior attributed to a decrease of the content in relation to the material in natura and its enrichment only in sample B550 °C. Authors such as Gunal *et al.* (2019), Gezahegn, Sain and Thomas (2019) and Kameyama, Iwata and Miyamoto (2017), noticed in their pyrolysis of different biomasses an increase of K levels behavior in relation to the increase in temperature. The same authors agree with the observation that some chemical components are concentrated in the solid phase of carbonized during the pyrolysis, also relating this behavior to the conversion of nutritional elements into oxides and carbonates, which raise the alkalinity of the material, and its high volatilization temperature (760-1240°C), according to Naeem *et al.* (2014).

Regarding the pH and the EC, the increase of the temperature caused the samples to become increasingly more alkaline and raise their EC. According to Joseph *et al.* (2009), the increase of the EC with the combustion temperature may be associated to the alignment of the aromaticity of the materials. In CEC, as previously mentioned, the increase of the temperature in the samples made their value lower, being more accentuated when comparing samples B450 °C (71 mmol/kg) and B550 °C (17 mmol/kg).

The acidity or alkalinity in the pH of biochars is related to the presence of organic functional groups (COOH and OH), carbonates and alkaline metals, which are also associated to the CEC. The predominance of organic functional groups maintains the material acid and its CEC reduced at lower temperatures. However, with the increase of the temperature, thermal decomposition and consequent degradation of the oxygenated functional groups, the alkaline functional groups stand out, increasing the basic properties of the surface. This increase in temperature also increases the anion-exchange behavior, resulting in an increase of the pH (HASSAN *et al.* 2020) and decreasing its CEC, according to what was observed in the analysis of the samples (JOSEPH *et al.*, 2009; GUARNIERI, 2016; YANG *et al.*, 2019; Guilhen, 2018).

3.3 Valorization potential of the carbonized coconut fibers as soil conditioners

The characterization of carbonized with agricultural purposes has combinations of each type of biomass, which makes the assertion of its potential complex, especially without considering an application in a specific soil.

Some properties analyzed, such as the ashes, in the carbonized may indicate a source of nutrients. High ash contents, as, for example, the biochar of maize straw pyrolyzed at 500 °C (17.6%) or Rhodes grass at 400 °C (28.80%), presented by Jafri *et al.* (2018), may reduce soil acidity and increase the concentration of elements such as Ca, Mg and K. However, they contribute for the decrease of FC levels (Novotny *et al.*, 2015; Andrade *et al.*, 2004). In addition to the ashes, the release of volatile material

in the pyrolysis causes unblocking of pores previously blocked by condensed volatiles. Higher porosity may be a place of nutrient deposition for the soil and interaction with microorganisms, which may be present in the samples that had a higher volatilization of fiber to carbonized, as is the case of sample B550 °C (Joseph *et al.*, 2009).

The results of the chemical analysis of the samples confirm the recalcitrant characteristic of the carbonized, with high TC values, even in the carbonized material at the lowest peak temperature. According to Rezende *et al.* (2011), the pyrolysis of biomasses at temperatures of 300 °C to 600 °C has as a consequence a material that degrades more slowly, creating carbon stocks in the soil in the long term, and its structures, increasingly similar to graphite, rich in C, maintain the recalcitrance of the carbonized, characterizing a more efficient carbon sequestration system.

Regarding the availability of nutrients contained in the carbonized produced, most elements had their content reduced. According to Chan and Xu (2009), elements such as P in biochars have an availability for plants of only 13% in relation to the total P, which is one of the most important and required nutrients for plants and is scarce in most Brazilian soils (Bibar, 2016). In another perspective, Downie, Crosky and Munroe (2009) pay attention to the risk of phyto and eco toxicity that high levels of chemical elements can provide to some plant species. Thus, the use of each carbonized must be carried out viewing the necessities of the soil and its target species.

According to the properties of the applied soil, the alkaline pH obtained in the samples can also have beneficial or adverse effect. Carbonized biomass with alkaline nature has a value of beneficial liming value for soils with acidic properties and may decrease the saturation of Aluminum, which are the main constraints for the production in highly weathered soils. This fact becomes relevant at the regional level since the soils in Rio Grande do Sul is considered quite acid (KAPPLER *et al.*, 2018).

The CEC of the analyzed carbonized is lower than what is found in some literatures. The highest value of the cation-exchange capacity analyzed was referent to sample B350°C (81 mmol/kg). Authors such as Angalaeeswari and Kamaludeen (2017) showed a value of 119.3 mmol/kg for analysis of coconut fiber carbonized at 450 °C for 2 to 3 hours, Wu *et al.* (2016), using the same material, found a value of 700 to 811.7 mmol/kg for pyrolyzed samples between 300 and 700 °C. Glaser *et al.* (2000) points out that the Indigenous Black Lands in the Amazon reached CEC values between 96 and 150 mmol/kg. The incorporation of biochar in soils promotes an increase in CEC (ALBERT *et al.*, 2020). An increase in the CEC has as one of its functions the adsorption of organic matter carried on the surface of the carbonized and to promote soil aggregation (MAJOR *et al.*, 2009).

In relation to EC, it becomes hard to find a line of

comparison in the literature, since the values sought are different from each other, not only in relation to green coconut fiber/husk, as in other biomasses. Conz (2015), who analyzed carbonized chicken manure, found an average between samples of 5512.7 $\mu\text{S}/\text{cm}$, whereas Schropfer (2018), in the analysis of carbonized rice husks had values varying between 21.03 to 44.18 $\mu\text{S}/\text{cm}$, thus the values found in the work may be considered high, always depending on application variables.

4. CONCLUSIONS

The results indicated that the coconut fiber has relevant properties for thermochemical conversion. The pyrolysis temperature influenced the characteristics of the obtained biochars, decreasing the yield of the solid fraction post pyrolysis, apart from providing greater obtainment of total and fixed Carbon. The X-RF showed that the carbonized presents K, Cl, Ca, Na and Mg content in its composition, in smaller concentrations than in the biomass in natura. The pH proved to be acidic for the biomass and alkaline for the carbonized, influenced by the increase of the temperature, which also increased the values of the EC and decreased the CEC.

The carbonized sample at 450 °C showed yield rates, chemical and physical composition considered more desirable when referring to a soil application since in most of the results the values had a behavior between the extremes. Additionally, they presented high levels of FC, which can be considered a beneficial property for all soils, both for the C storage, as well as for maintaining agronomic effects to last longer in the soil.

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GK: Formal analysis and Writing – review & editing.

RCEM: Resources, supervision and Writing – review & editing.

CAMM: Project administration, funding acquisition, resources, Writing – review & editing, conceptualization and supervision.

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