

Original Research Article

Sugarcane Biochar for Agricultural Use Produced in Different Conditions of Pyrolysis

ABSTRACT

From the pyrolysis process, biochar is a carbonrich and recalcitrant organic material with potential for longterm carbon sequestration because of its aromatic structure. However, the physical and chemical properties of the biochar vary due to the diversity of raw material and the conditions of production. The present study aimed to evaluate the biochar from the sugarcane bagasse at different temperatures and under two conditions of pyrolysis. The biochar was produced at two final temperatures 200°C (1 hour); 250°C (1h) and 250°C (2h), with pyrolysis of an oxidizing and non-oxidizing atmosphere for both. PH, cation exchange capacity (CTC), carbon content (C), Nitrogen (N), hydrogen (H), H:C, C:N and ash ratios were evaluated. The contents of C, H, N and the atomic ratios H:C and C:N were higher in Biochar produced in a non-oxidizing atmosphere(BNO). However, the content of ash, pH and CTC were higher in Biochar produced in oxidizing atmospheres (BO). One can conclude the direct influence of the pyrolysis condition.

Keywords: Biochar, Carbon, Pyrolysis, Sugarcane.

1. INTRODUCTION

Brazil is the largest producer of sugarcane in the world, with an area of approximately four million ha⁻¹ under cultivation of this species (*Saccharum sp.*) And according to [1], in the 2017/18 crop, Brazil's sugarcane production was of the order of 633.3x10⁶ MG. The amount of bagasse contained in one tonne of sugar cane varies between 195 kg [2] and 315 kg [3]. Thus, in the worst condition, production of sugarcane bagasse is estimated for the 2017/18 crop, of the order of 123.49x10⁶ MG. The amount of sugarcane bagasse available is enormous, and even though most of it is burned in the power generation by the mill, there is a large surplus that can be used for various purposes.

Sugar cane residues, when not managed, can increase the risk of pollution to the environment, but when properly utilized they can significantly reduce the production costs of the sugar and ethanol matrix and the risks of environmental damage [5]. One way of using the waste is the production of biochar, from sugar cane bagasse, for incorporation into the agricultural soil. Biochar is the product resulting from pyrolysis (thermal decomposition) of biomass where the presence of oxygen is limited and its production can be obtained in various ways, with the variation of the atmosphere and the temperature of the combustion environment, as well as the time and the combustion gear [6].

Recent studies have shown that biochar can be used in agricultural soil to sequester carbon [7 and 8], reduce greenhouse gas emissions [7] and improve nutrient retention and crop yield [9 and 10]. According to [11], one of the answers to the potential of enriching soils with biochar is that charcoal is porous, so that it acts as a sponge by retaining water and nutrients dissolved in it, something that poor soils do not efficiency.

In a study conducted by [12], it was found that bamboo biochar interferes with the water retention capacity. The aromatic structure of the biochar, which has hydrophobic characteristics, can reduce the penetration of water into the porous spaces of the soil aggregates, thus increasing the stability of the aggregates [13]. However, the variations in the pyrolysis process greatly influence the quality of the biochar [6]. The objective of this work was to evaluate the potential, for agricultural purposes, of the biomass of the sugarcane bagasse produced under different conditions of low temperature pyrolysis.

2. MATERIAL AND METHODS

The sugarcane bagasse, originating from the Libra Alcool plant, located in the municipality of São José do Rio Claro, MT, was made available by the Interuniversity Network for the Development of the Sugarcane Sector. This material was stored in raffia bags in a covered, ventilated and dry environment. Biochar was produced in the Food Technology laboratory of the Faculty of Agronomy and Animal Science of the Federal University of Mato Grosso from January to September, 2017. Two processes of pyrolysis were used in the production of the biochar: Oxidizing Atmosphere and Non-Oxidizing Atmosphere saturated with nitrogen). The experimental design was completely randomized (DIC) in a 2x3 factorial scheme, with two pyrolysis conditions (oxidizing and non-oxidizing) and three pyrolysis operations. The sugarcane bagasse (biomass), in the oxidizing condition, was packed in two refractory ceramic vats, each with a capacity of approximately 50 g. The material was then taken to a muffle-type electric oven to proceed to pyrolysis. The treatments (marches) in the oxidizing condition were as follows: 200°C for 2 hours (BO200-2h); 250°C for 1 hour (BO250-1h) and 250 ° C for 2 hours (BO250-2h). In the non-oxidizing condition the bagasse was conditioned in a combustion chamber with lid and gas inlet (Figure 1), made of AISI 304 stainless steel, wall thickness of 1.25 mm (sheet 18). The chamber was used to optimize the amount of nitrogen used in this process. After filling with bagasse (about 120 grams), the chamber was saturated with nitrogen by forced inflation, closed, taken to the muffle and subjected to the following pyrolysis marches: 200 ° C for 2 hours (BNO200-2h); 250Å°C for 1 hour (BNO250-1h) and 250Å°C for 2 hours, (BNO250-2h).

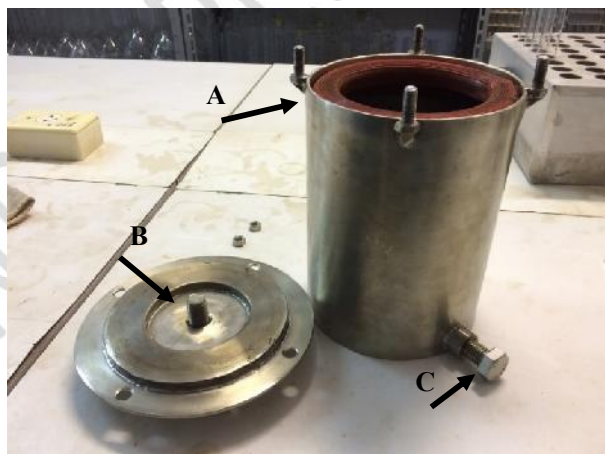


Fig. 1. Inox chamber used for pyrolysis in the non-oxidizing condition. A: Cap seal; B: N2 input; C: Chamber air outlet, Cuiabá, Mato Grosso, Brazil

The treatments resulting from the combination of the two pyrolysis conditions and different gears are found in Table 1.

Table 1. Temperature and time of carbonization according to the gear and pyrolysis conditions

Treatment	Kind of Pyrolysis	Running time at each temperature (°C)					Final time
		50	100	150	200	250	
BNO200-2h	N oxidant	1h	1h	1h	2h	-	2h
BNO250-1h	N oxidant	1h	1h	1h	1h	1h	1h
BNO250-2h	N oxidant	1h	1h	1h	2h	2h	2h
BO200-2h	oxidant	1h	1h	1h	2h	-	2h
BO250-1h	oxidant	1h	1h	1h	1h	1h	1h
BO250-2h	oxidant	1h	1h	1h	2h	2h	2h

BNO: Biochar produced in a non-oxidizing atmosphere; BO: Biochar produced in oxidizing atmospheres.

The humidity of the sugarcane bagasse, to express the results obtained in dry basis, was determined by means of the initial mass and the dry mass obtained after drying in an oven with forced circulation at 65°C for 72 hours, until reaching constant mass [14].

The determinations of the gravimetric yield were made by gravimetry and expressed as a percentage of dry basis, taking the mass of the biochar produced and the sugar-cane bagasse used in its production before being submitted to the pyrolysis process. The ash content was obtained by the mass of the sample before and after being submitted to the muffle furnace at 550°C for 4 hours. The volatile solids content (SV) of the bagasse was also determined by gravimetry. For determination of pH, 5 g of biochar were weighed and diluted in 75 mL of the 0.01 mol L⁻¹ CaCl₂ solution. The analysis of cation exchange capacity (CTC) was performed according to the Manual of Official Analytical Methods for Fertilizers and Corrective Agents [15].

The determination of the elemental C, H and N was carried out on samples of approximately 1.0 mg of dry mass of biochar inserted into specific tin capsules for the 680 Series elemental analyzer (LECO Corporation World Headquarters, St. Joseph, MI, USA), described in [16]. The carbon / nitrogen (C:N) and hydrogen/carbon (H:C) ratios were calculated from the results obtained in the elemental analysis.

Statistical analysis of the results was performed using SISVAR software. Data were submitted to analysis of variance (ANOVA) and means were compared by the Scott-Knott test at the 5% level of significance.

3. RESULTS AND DISCUSSION

The yield for the oxidative condition of production presented decreasing values with the increase of the pyrolysis temperature, but not different ones, showing that in the presence of oxygen, even at low temperatures (200°C), the loss of volatile compounds is great (Table 2), when compared to the production in non-oxidizing condition. The BO had a yield lower than the BNO, regardless of the pyrolysis temperature. It is understood that this value is justified, due to the pyrolysis atmosphere.

Table 2. Gravimetric yield (%), pH and CTC (cmmolc kg⁻¹) of sugarcane bagasse biochar produced under different pyrolysis conditions

Attribute parsed	Pirolise Condition	Temperature (°C)/Residence time (h)		
		200/2	250/1	250/2
Gravimetric Yield	BNO	89,14 Aa	72,93 Ab	70,60 Ab
	BO	35,00 Ba	29,87 Ba	25,67 Ba
pH	BNO	4,20 Ac	4,46 Ab	4,66 Aa
	BO	3,40 Ba	3,30 Ba	3,33 Ba
CTC	BNO	49,00 Ab	53,66 Ba	37,33 Bc
	BO	47,33 Ac	177,33 Ab	182,33 Aa

BNO: Non-oxidizing biochar, BO: Oxidizing biochar. Means followed by the same capital letter in the column or lowercase in the row for the same attribute do not differ statistically by the Scott-Knott test at the 5% error probability level.

The biochar yield in the condition of non-oxidizing pyrolysis, unlike the oxidizing condition, was affected by the pyrolysis temperature, being lower when this was higher. At a temperature of 200°C the yield was better, 89.14%. [17] studied colza biofuel at various temperatures and obtained 80% yield at 200°C and 20% at a temperature of 700°C. Such occurrence is a result of the loss of volatile substances in a gradual way, so that the loss is proportional to the pyrolysis temperature.

The biochar yield in the present work was not affected by increasing residence time from one to two hours at 250°C for the same pyrolysis condition. In the studies of [18], with temperatures and residence times, the yield of sugarcane bagasse bioaccumulated, remained close to 88% for 20 minutes and decreases linearly to somewhere around 84% for 60 minutes residence in the pyrolysis at 200°C. At 250°C the decline was more pronounced, decreasing from approximately 72% to 52% in the same residence times. For higher temperatures the decline was exponential.

The ash content found for the sugarcane bagasse used in this work was 4.69 ± 0.79 , on a dry basis. Values of 4.33%, and 4.98% and 2.52%, were found, respectively by [19] and [18]. Variations in ash content may occur due to several factors, such as the age and variety of the sugarcane that originated the bagasse, determination methodology and calculation basis used to express the results. The average ash values of the biochar produced showed significant differences for the pyrolysis condition, with the ash content being higher for BO, with 15.84%, while the BNO had the lowest amount of ashes, 4.67%. There were no differences between the temperatures and residence time studied for the same pyrolysis condition. With the increase of the pyrolysis temperature it leads to the decomposition of the volatile solids and, on the other hand, concentration of the minerals in the biochar. The high value of the ash content of the BO, in relation to the BNO, is justified because of its high carbonization in the oxidizing atmosphere, when more volatile compounds were lost, with consequent accumulation of mineral compounds. The ash content obtained by [20] for bioaccumulation of the sugarcane bagasse with pyrolysis at 400 ° C was around 10% and, as the pyrolysis temperature increased, the ash content increased and the content of matter volatile matter decreased not only for sugarcane bagasse biochar, but for all seven raw materials studied.

The total of volatile materials found for the sugarcane bagasse used was $95.31\% \pm 0.79$, on a dry basis. The volatile materials are eliminated during the carbonization process and are formed by carbon, hydrogen and oxygen. Volatile bagasse values of the order of 75.03% were found by [21].

The values obtained for pH, found in Table 2, are all lower than 4.7, demonstrating that the obtained bio-cores are acidic. However, differences in pH values are observed, depending on the environment and the pyrolysis time / temperature. The BO obtained values of pH between 3.3 and 3.4 being not different when the conditions of pyrolysis and temperatures were modified. The bioaccum produced in modified atmosphere, saturated with N₂ (BNO), present higher pH values than those produced in the oxidizing atmosphere (BO), for all time / temperature combinations studied. The pH values for the BNO were different and increasing, between 4.20 and 4.66, with the increase of the pyrolysis temperature. The elevation of the temperature promotes the increase of the pH, once, when raising the temperature of pyrolysis, the formation of carbonates is promoted and the decrease in the acid groups greater accumulation of ashes.

In the present study, the pyrolysis time, in the non-oxidizing condition, also influenced the pH, since the value obtained with 2 hours of pyrolysis was higher than that obtained with one hour at 250°C. The author cited in reference [22] found pH of 5.39 for two hours of pyrolysis of sugarcane bagasse at 300 ° C. In their research [20] found pH close to 5 for pyrolysis at 400°C for 2 hours, but the values were increasing with the pyrolysis temperature increase. The pH value in the study of rapeseed biomass increased rapidly with the pyrolysis temperature from 200°C, but tended to stabilize at temperatures above 500°C [17].

These results confirm that under conditions of non-oxidizing atmosphere, for the same temperature, biochromes with higher pH are produced when the pyrolysis time is longer.

The CTC determined in the biochar varied according to pyrolysis conditions and temperatures (Table 2). The CTC value was higher in BO when compared to BNO, at temperatures of 250-1h and 250-2h, with 177.33 and 182.33 cmol kg⁻¹, respectively. It can be justified by the indirect way of obtaining this property, which considers the increase in the concentration of exchangeable cations such as calcium, magnesium and potassium [23 and 24]. In their research [25] has shown to have a higher degree of functional groups of oxygen surface, resulting in an increase of COC of biochar.

Biochars can potentially increase the cation exchange capacity (CEC) of soils, especially for highly weathered and nutrient poor sandy soils; however, this depends on the properties of the bio-bio and the aging of the biocharapplied to the soil.

The CTC increases as the pyrolysis temperature increases. This increase in temperature is responsible for the removal of volatile material, composed of the acidic functional groups present in the structure of the biochar resulting in CTC [26]. However, it was not similar to the expected result in this work. CTC values decreased as the temperature increased. [24] producing biochar from wood of the white lead trees (*Leucaena leucocephala*) at 700°C CTC was obtained in the amount of 22.3 cmol kg⁻¹.

The literature states that biofuels from woody materials provide low CTC values, while non-woody materials tend to have high CTC values [27]. However, it is important to highlight that even with reduced CEC, the biochar has greater persistence in the soil and can contribute to the CTC of the medium for a longer time when compared to its raw material of easy degradation.

The elemental contents of carbon (C), hydrogen (H), nitrogen (N), atomic H: C and C: N atomic ratios of biofuels are presented in Table 3. The values were influenced, according to the temperatures and pyrolysis conditions. The total content of C was 50.53% for BNO and 58.79% for BO, being the treatment of greater accumulation of C, differing from the literature, which result in an increase of C with increasing temperature [28]. Result different from that found by [29] producing biochar from the bagasse at the temperature of approximately 500°C with 54.84%. The carbon content of the biochar at 500°C was 79.42% on a dry basis, representing 48.36% by weight of carbon in the crude biomass. This implies that the biochar becomes more and more concentrated in carbon at high temperatures, releasing H and O. Lignin-rich raw materials produce biochar with higher

Carbon. The sugarcane bagasse contains approximately 30% of lignin, producing biochar with C contents in the range of 63 to 84% in pyrolysis of 600°C [30].

Table 3. Elemental content, in percentage, of sugarcane bagasse biochar produced by different pyrolysis conditions

Biochar	Content				
	C (%)	H (%)	N (%)	H/C	C/N
BNO	50,53 B	5,14 A	0,34 B	0,10 A	146,93 A
BO	58,79 A	2,00 B	0,82 A	0,03 B	74,77 B

BNO: Non-oxidizing biochar BO: Oxidizing biochar. Averages followed by the same capital letter in the column or lowercase in the row do not differ statistically by the Scott-Knott test at the 5% error probability level.

The content of H, different from C, was higher in BNO with 5.14% (Table 2). The BNO promoted greater accumulation of H, it is generally expected that in the process of pyrolysis, independent of the raw material, losses of H can be attributed to the breakage of weaker bonds in the structures of biochar. Close results were found by [31], with a H content of 6.01 producing biochar from fir wood at a temperature of 200°C for six hours. The carbon content increased while the H content decreased, which corresponds to an increase in carbon. This observation indicates that the degree of carbonization in BO was accelerated [32].

Biocarbon showed low values of N (Table 3), for BNO and BO, with 0.34 and 0.82%, respectively. [29] producing bagasse at the temperature of 500°C for 1 h, obtained 1.11 of N.

Biomass pyrolysis at high temperatures (> 200°C) produces biochar highly resistant to biological degradation due to the increase in recalcitrance, ie low H: C ratio. The most recalcitrant biochar is BO, with a ratio of 0.03%. The proportion of aromatic C increases due to the relative increase in the loss of volatile material (initially water, followed by hydrocarbons, tar fumes, H₂, CO and CO₂) and its high ash content. While the thermal degradation of the biomass continues in roasting, the mechanisms of decarbonization, dehydrogenation and deoxygenation occur [32] and, therefore, the H:C ratios decrease when the temperature is high [18].

The C: N atomic ratio for BNO was 146.93, being higher in relation to the 74.77 obtained for the BO 74.77, indicating that in the absence of oxygen the fixation of C is greater. The C: N ratios found by [18] and [22] were, respectively, 159.4 and 193.6 for pyrolysis temperatures of 250 ° C and 300 ° C. The C: N ratios for sugarcane bagasse found by [21] and [18] were, respectively, 92.8 and 55.6. As the pyrolysis temperature increases, C-rich and N-poor compounds are usually formed, as this is quite volatile. The increase in the C/N ratio is evidence of the production of compounds with high levels of stable [33].

4. CONCLUSION

The pyrolysis condition modifies the characteristics of the biochar. The non-oxidizing biochar contains a higher gravimetric yield, elemental concentration at different temperatures and a higher H: C and C: N ratio, which indicate an increase in the recalcitrance of the organic material. Oxidant biochar oil contains higher pH and CTC.

In short-term experiments there are no responses of the biochar action from the sugarcane bagasse, in the conditions of oxidizing and non-oxidizing pyrolysis of 200°C

and 500°C in the physical-water properties in the sandy soil. However, the non-oxidizing biochar produced at 500°C retains a higher water content due to its lower hydrophobicity.

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