UNIVERSIDADE FEDERAL DE SÃO CARLOS

CENTRO DE CIÊNCIAS E TECNOLOGIA PARA A SUSTENTABILIDADE

PROGRAMA DE PÓS-GRADUAÇÃO EM

PLANEJAMENTO E USO DE RECURSOS RENOVÁVEIS

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Tese apresentada ao Programa de Pós-Graduação em Planejamento e Uso de Recursos Renováveis para obtenção do título de Doutora em Planejamento e Uso de Recursos Renováveis.

Orientação: Prof. Dr. Fábio Minoru Yamaji
Coorientação: Prof. Dr. Hiroyuki Yamamoto
Financiamento: CAPES

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2020

# GABRIELA TAMI NAKASHIMA

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Universidade Federal de São Carlos
Sorocaba, 29 de maio de 2020

Certifico que a sessão de defesa foi realizada com a participação à distância dos membros Prof. Dr. Hiroyuki Yamamoto (Coorientador – Universidade de Nagoya), Dra. Mariana Provedel Martins (Evonik), Dra. Miyuki Matsuo (Universidade de Nagoya), Profa. Dra. Luciana Camargo de Oliveira (UFSCar Sorocaba), Prof. Dr. Giovanni Pimenta Mambrini (UFSCar Sorocaba) e Prof. Dr. João Lúcio de Barros (IFSP). Depois das arguições e deliberações realizadas, os participantes estão de acordo com o conteúdo do parecer da comissão examinadora redigido no relatório de defesa de Tese de Gabriela Tami Nakashima.

**Prof. Dr. Hiroyuki Yamamoto (coorientador)**
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# AGRADECIMENTOS

*"No matter how many times the results of experiments agree  with some theory, you can never be sure that the next time the result will not contradict the theory."*

*Stephen Hawking*

# RESUMO

NAKASHIMA, Gabriela Tami. *Produção, melhorador do solo e sustentabilidade do biochar de palha de cana-de-açúcar*. 2020. Tese (Doutorado em "Planejamento e uso de recursos renováveis") – Centro de Ciências e Tecnologias para Sustentabilidade, Universidade Federal de São Carlos, Sorocaba, 2020.

Antigamente, a colheita da cana-de-açúcar era realizada manualmente com auxílio de fogo para facilitar o corte. A Lei do Estado de São Paulo n° 11.241, de 19 de setembro de 2002, que estabeleceu o fim do uso da queima da palha da cana-de-açúcar que, com isso, passou a ser um resíduo nos plantios. Para dar um melhor destino a este resíduo, algumas alternativas estão sendo estudadas como a utilização na produção do biochar. O biochar é um produto da pirólise da biomassa, rico em carbono, que possui qualidades como condicionador do solo. Neste contexto, os objetivos deste estudo foram: verificar as melhores condições (temperatura de pirólise e tempo de residência) para a produção de biochar de palha de cana-de-açúcar e sua caracterização (capítulo 2), como a biodegradação deste biochar influencia no sequestro de carbono (capítulo 3) e o desenvolvimento de mudas de cana-de-açúcar com a adição de porcentagens de biochar aplicados em solo (capítulo 4). Para verificar as melhores condições de produção do biochar (cap.2), foram escolhidos 6 tratamentos, com 3 diferentes temperaturas de pirólise e 2 tempos de residência: 200 °C – 2 horas, 200 °C – 4 horas, 325 °C – 2 horas, 325 °C – 4 horas, 450 °C – 2 horas, 450 °C – 4 horas. Os tratamentos foram submetidos à análise imediata, rendimento gravimétrico, porosidade, análise termogravimétrica (TGA), análise de espectroscopia de infravermelhos com transformadas de Fourier (FTIR), análise de difração de raios-X (DRX) e análise de hidrofobicidade. Para biodegradação do biochar (cap.3) os tratamentos foram: palha de cana-de-açúcar *in natura*, 200 °C – 2 horas, 325 °C – 2 horas, 450 °C – 2 horas. Estes biochar foram caracterizados pela sua composição elementar (C - carbono, H - hidrogênio, N - nitrogênio). Para verificação da influência do biochar no sequestro de carbono, foram quantificados os gases $CH_4$, $CO_2$ e $NO_2$ durante um período de 85 dias, sendo uma coleta por semana. Para o experimento em vasos (cap. 4), o biochar foi incorporado ao solo em diferentes dosagens, simulando: 0 ton $ha^{-1}$, 1 ton $ha^{-1}$, 5 ton $ha^{-1}$, 15 ton $ha^{-1}$, 30 ton $ha^{-1}$. Foram instaladas 15 parcelas para cada dosagem, totalizando 150 plantas (vasos). As medições de altura e diâmetro das canas-de-açúcar foram coletadas a cada 20 dias durante 9 meses. Ao final do experimento, foi obtida a massa seca da parte aérea e das raízes. O solo utilizado foi analisado quimicamente antes e depois do experimento em vasos. Os resultados da caracterização dos biochar produzidos pelo Cap. 2, mostraram que a temperatura de pirólise foi um fator que tem mais influência nas características finais do biochar do que o tempo de residência. No Cap. 3, foi observado que as maiores taxas de emissões de gases do efeito estufa (GEE) foram liberadas pelos tratamentos com a palha *in natura* e com o biochar 200 °C, sendo os tratamentos a 325 °C e 450 °C mais estáveis e resistentes a biodegradação. No Cap. 4, a incorporação do biochar não resultou em melhoras no crescimento da cana-de-açúcar, mas influenciou no aumento do pH do solo. De um modo geral, o biochar de 325 °C com 2 horas de tempo de residência apresentou resultados suficientes para sua aplicação no solo. O biochar ainda se mostrou uma alternativa viável para a redução da emissão de GEE.

Palavras-chave: Biocarvão. Biomassa. Aplicação no solo. Fixador de carbono.

# ABSTRACT

NAKASHIMA, Gabriela Tami. *Production, soil amendment and sustainability of sugarcane trash biochar*. 2020. Thesis (Doctorate in "Planning and use of renewable resources") – Centro de Ciências e Tecnologias para Sustentabilidade, Federal University of São Carlos, Sorocaba, 2020.

In the past, sugarcane was harvested manually with the aid of fire to facilitate cutting. And because of the Law of the State of São Paulo n. 11,241, which establishes the end of the use of the burning, the sugarcane trash that was previously burned, today is a residue in the plantations. To add value and give a better destination to this residue, some alternatives for its use as raw material are studied. Biochar is a product of pyrolysis of biomass, rich in carbon, which has qualities as a soil conditioner. Therefore, the objectives of this thesis were: to verify the best conditions (pyrolysis temperature and residence time) for biochar production of sugarcane straw and its characterization (Chapter 2), how the biodegradation of this biochar influences for carbon sequestration (Chapter 3) and check the development of sugarcane seedlings with the addition of percentages of biochar in soil (Chapter 4). To verify the best conditions for biochar production (Chapter 2), 6 treatments with 3 different pyrolysis temperatures and 2 residence times were chosen: 200 °C - 2 hours, 200 °C - 4 hours, 325 °C - 2 hours, 325 °C - 4 hours, 450 °C - 2 hours, 450 ° C - 4 hours. The treatments were submitted to proximate analysis, gravimetric yield, porosity, thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy analysis (FTIR), X-ray diffraction analysis (XRD) and hydrophobicity test. For biochar biodegradation (Chapter 3), the treatments were: sugarcane straw *in natura*, 200 °C - 2 hours, 325 °C - 2 hours, 450 °C - 2 hours. These biochars were characterized by their elemental composition (C - carbon, H - hydrogen, N - nitrogen). The biochar (6.3 g/flask) was incubated in 4 flasks by treatment with characterized soil. The quantification of the gases ($CH_4$, $CO_2$, $NO_2$) was performed to verify the influence of biochar on carbon sequestration will occur in a period of 85 days, one sampling per week. For pot experiment (Chapter 4), the biochar produced at 330 °C - 1 hour was mixed to the soil in different application rates: 0 t $ha^{-1}$, 1 t $ha^{-1}$, 5 t $ha^{-1}$, 15 t $ha^{-1}$, 30 t $ha^{-1}$. It was installed 15 plots per dosage/treatment, totalizing 150 plants. Height and diameter measurements were collected every 20 days for 257 days. At the end of the pot experiment it was obtained the dry mass of the aerial part and roots. The soil used was analyzed chemically before and after the pot experiment. The results of the characterization of the biochar produced by Chapter 2, showed that the pyrolysis temperature was a factor that has more influence on the final characteristics of the biochar than the residence time. In Chapter 3, it was observed that the highest rates of greenhouse gas (GHG) emissions were released by treatments with *in natura* and with biochar 200 ° C, with treatments at 325 °C and 450 °C being more stable and resistant to biodegradation. In Chapter 4, the incorporation of biochar did not result in improvements in the growth of sugarcane but did influence the increase in the pH of the soil. In general, the 325 °C biochar with 2 hours of residence time showed enough results for its application to the soil. Biochar has also proved to be a viable alternative for reducing GHG emissions.

Keywords: Biochar. Biomass. Soil application. Carbon fixation.

**SUMÁRIO**

## CHAPTER 1 – LITERATURE REVIEW

### 1.1. INTRODUCTION

In Brazil, sugarcane (*Saccharum officinarum* L.) is a crop that has been studied because it has economic importance with its by-products (sugar and ethanol). Along with the sugar and ethanol production process, many residues are generated. The most known, the bagasse is being already used in energy cogeneration and in the 2nd generation ethanol. Another residue is straw or trash, which is considered a new residue due to the mechanization of the sugarcane harvest.

The reuse of sugarcane trash has been applied in several trials (GÓMEZ et al., 2014; HASSUANI; LEAL; MACEDO., 2005; LEAL et al., 2013). One of the first attempts was simple use as a protector for the soil. But the large amount of waste left in the soil created an ideal habitat for fungi and insects that harmed the sprouts. Another trial use was for energy as direct burning. But, the high contents of inorganic components in sugarcane trash cause fouling and slagging in the boiler, increasing the maintenance cost. The biochar production could be an alternative for the sugarcane trash.

Biochar is one of the products from pyrolysis. It has the same process to produce charcoal, but the use of biochar is mainly for soil application. Biochar is a carbon-rich material that, recently, has become more studied due to its characteristics.

The background for this study is shown this chapter (Chapter 1). The characteristics of sugarcane trash biochar are described on Chapter 2. The utilization of biochar due to its potential mitigation of greenhouse gases (GHG) emissions is seen in Chapter 3. And, the application of biochar on fields, the interaction between soil and biochar and its effects on crop yield are described in Chapter 4.

### 1.2. SUGARCANE

Sugarcane was introduced in Brazil around year 1500 with the Portuguese colonization. Since then, sugarcane had a huge participation in Brazilian history. Because of soil and climate conditions, sugarcane had a good adaptation and could spread in Brazilian territory (UNICA, 2004). Nowadays, Brazil is the major producer of sugarcane, with a planted area of 8.5 million ha and estimated productivity of 75,783 kg ha$^{-1}$ for the 2019/20 harvest crop season (CONAB, 2019).

Sugarcane is one type of grass, that belongs to Poaceae family and its genus is *Saccharum* L. (TOPPA et al., 2010). *Saccharum* spp. is consider a C4 plant (MARIN; NASSIF, 2013). The C4 classification is related to carbon fixation, it is common in monocots (grasses and sludges) and has more efficiency in greater conditions of light and temperature (EHLERINGER; CERLING, 2002).

The constituents of sugarcane *in natura* are stem and green leaves (8%), sheath and dry leaves (20%), clean stalk (72%) (GÓMEZ et al., 2014). The main products of sugarcane are sugar and ethanol, which are extracted from sugarcane stalk. The expected production for 2018/19 is 30.1 million tons of sugar and 35.5 billion liters of ethanol (CONAB, 2019).

Due to the greatness of the cane numbers, its importance to the agribusiness and by the large interest in biofuels, many researches have explored this material. There are studies involving sugarcane botany (DILLEWIJN, 1952), pests' control (DINARDO-MIRANDA; COELHO; FERREIRA, 2004; MADALENO et al., 2008), residue recovery system (MICHELAZZO; BRAUNBECK, 2008; MUNDIM; PELISSARI; PEREIRA, 2009; RIPOLI; GAMEIRO, 2007, second generation ethanol (2G ethanol) (DIAS et al., 2011; OLIVEIRA et al., 2013; OLIVEIRA et al., 2014; PEREIRA et al., 2016; SANTOS et al., 2012; SANTOS et al., 2014; SILVA et al., 2010), bagasse for energy (HOFSETZ; SILVA, 2012), storage (NAKASHIMA et al., 2017; SANTOS et al., 2011), trash use (GÓMEZ et al., 2014; HASSUANI; LEAL; MACEDO., 2005; LEAL et al., 2013), solid biofuel (ALÓ et al., 2017; BRASIL et al., 2015; JITTABUT, 2015; NAKASHIMA et al., 2017; SILVA et al., 2015; ) and biochar (JEONG; DODLA;WANG., 2016; RÓZ et al., 2015).

## 1.3. SUGARCANE TRASH

Sugarcane trash includes green leaves, dry leaves and the tops. Sugarcane production generates 14 t ha$^{-1}$ of residues. In the past, 85% sugarcane trash used to be burned to facilitate and to reduce the cost of harvesting (HASSUANI; LEAL; MACEDO, 2005).

After Federal Decree no. 2661 of July 9, 1998 and São Paulo State Law no. 11241 of September 19, 2002, the farmers had to adjust the harvest without using previous burning. Thereby, it was needed a mechanization during the harvesting operation, remaining the straw on the field. Silva et al. (2012) concluded that a percentage of sugarcane trash is necessary to remain on the field to avoid erosion, water loss, organic matter and nutrient losses. However, the other part can be used to aggregate value to this trash. An alternative is trash recovering for energy or other uses such as biochar production.

## 1.4. BIOMASS CONVERSION

There are some routes to convert the biomass into biofuel: thermochemical, biochemical and chemical conversion (Fig. 1). Chemical conversion involves the esterification process, that is a reaction between a fat or oil, an alcohol and an alkaline catalyst. The main product obtained by this process is biodiesel. Biochemical conversion uses raw materials with high moisture content and room temperatures, throughout digestion process that it is possible to get biogas and fermentation process can result in ethanol. Thermochemical conversion is used to recover energy using high temperatures and feedstocks with low humidity (or moisture content). The processes are: combustion that generates steam for energy; gasification that results in syngas and pyrolysis that can provide syngas (gas), tar (liquid) and char (solid) (BNDES; CGEE, 2008; WEC 2016).

Figure 1. Biomass conversion technologies pathways
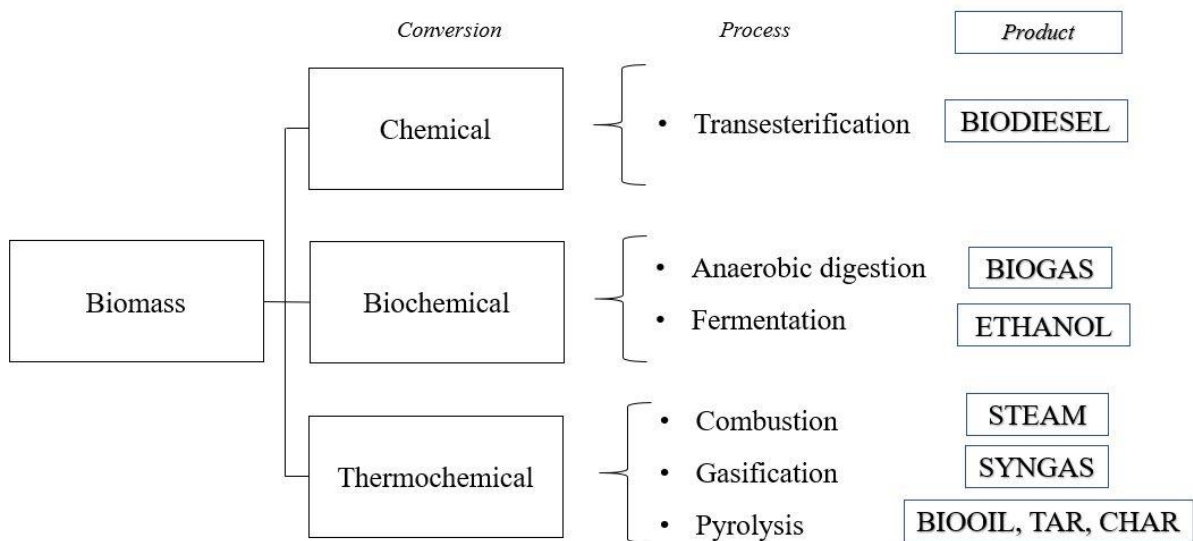


## 1.5. PYROLYSIS

Pyrolysis is a thermal degradation of an organic material without oxygen or partially without oxygen. The pyrolysis reaction can be demonstrated as (CHA et al., 2016; DEMIRBAS; ARIN, 2002):

$$Biomass + Heat \rightarrow Char + Volatiles \text{ (gases and liquids)}$$

Pyrolysis is a versatile technology that make possible convert lignocellulosic biomass into solid, liquid and gas products, according to chosen method (ROY and DIAS, 2017). The

methods are present in Table 1: fast pyrolysis, intermediate pyrolysis, slow pyrolysis and gasification (DUKU et al., 2011; IEA, 2007; SOHÍ et al., 2010).

Table 1. General conditions and products yield for dry wood basis obtained from different pyrolysis of wood.

| Mode | Conditions | Liquid | Char | Gas |
|---|---|---|---|---|
| Fast | Moderate temperature, around 500 °C, short hot vapor residence time ~1 second | 75% | 12% | 13% |
| Intermediate | Moderate temperature, around 500 °C, moderate hot vapor residence time ~10-20 seconds | 50% | 20% | 30% |
| Slow (carbonization) | Low temperature, around 400 °C, very long residence time (hours/days) | 30% | 35% | 35% |
| Gasification | High temperature, around 800 °C, long vapor residence time | 5% | 10% | 85% |

Source: IEA (2007).

Biomass *in natura* is a biodegradable material and pyrolysis can provide a new organization of remaining molecules with the loss of volatile matter and transform biomass in a more stable material (biochar). This reaction occurs between 200 and 500 °C (MCLAUGHLIN et al., 2009).

Fast pyrolysis and others pyrolysis technologies, that require short residence time, convert the biomass mostly in liquid form (GARCIA-PÉREZ, 2008; YAMAN, 2004). There are some parameters for the fast pyrolysis, such as the use of fine particles, controlled pyrolysis temperature around 500 °C, short hot vapor residence time (< 2 seconds) and rapid cooling (IEA, 2007).

Slow pyrolysis process needs longer residence time and occurs under oxygen-free conditions (SOHÍ et al., 2010). However, this process has lower risks to produce dioxins and polyaromatic hydrocarbons (PAH) and low temperatures can provide more aromatic carbon (BARROW, 2012).

## 1.6. BIOCHAR

Lehmann and Joseph (2009) described biochar as a "carbon-rich product obtained when biomass, such as wood, manure or leaves, is heated in a closed container with little or no available air". For McLaughlin et al. (2009) the "biochar is a term used to designate charcoal destined for addition to soils". Weber and Quicker (2018) defined biochar as the solid product

of biomass pyrolysis, that has been produced and utilized for several thousand years and is best known as charcoal (when produced from woody biomass).

Therefore, biochar is a thermally modified biomass, presenting more stable carbons. And its composition is generally formed by carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulfur (S) and ashes (DUKU et al., 2011). For these characteristics, biochar is known as soil improver and a carbon sequestration. Biochar can be produced by any type of organic feedstocks and under different pyrolysis conditions. The application will depend on the resulting properties obtained by feedstock or pyrolysis process (VERHEIJEN et al., 2010). There are a range of feedstocks that can be used to produce biochar. Almost all uncontaminated organic materials, such as "crop residues, bark, stem timber (logs), non-stem logging residues (bark, branches, tree-tops), various grasses and agricultural plant residues" (MATOVIC, 2011).

There are several studies cover the approaching the principles and parameters for biochar production (TOMCZYK; SOKOLOWSKA; BOGUTA, 2020). Duku et al. (2011) reviewed the biochar potential in Ghana focusing in soil application and Matovic (2011) explored a global and Canadian perspective about biochar, mainly for carbon sequestration. And, Matovic (2011) believes that Canada has a potential for biochar production, because of the diversity of the biomass sources. Barrow (2012) studied about biochar potential and its problems. He concluded that biochar production could be an alternative to reduce the use of fertilizers and has sequester carbon and soil amendment skills. On the other hand, problems to define the exact nature of biochar and the lack of standards can discourage or make misunderstanding during data interpretation.

Study with sugarcane and rice harvest residues using four different pyrolysis temperatures (450 °C - 750 °C) for 2 hours, had an increase in chemical functionality of biochar when the temperature raised. Treatments at 550 °C showed the best result for cation exchange capacity (CEC), presenting a good potential as soil amendment. The study also reveals that, in general, increasing pyrolysis temperature improves the water holding capacity (JEONG; DODLA; WANG, 2016).

## 1.6.1. Characterization

Feedstock and the conditions of production of biochar may influence the characteristics of the final product (CHAN et al., 2007; FRIEDMAN; TREADWELL; WILKI, 2012; JUNG; PARK; KWON, 2019; TOMCZYK; SOKOLOWSKA; BOGUTA, 2020). Windeatt et al. (2014) studied biochar from eight crop residues fixing de pyrolysis conditions at 600 °C. The

biochar yields obtained varied of 28 to 39% and pH results were from 6.1 to 11.6. They concluded that different results were attributed to feedstock variation.

Therefore, the characterization of biochar properties is an essential step in performing any type of work (SINGH; SINGH; COWIE, 2010). Proximate analysis and ultimate analysis are basic characterization for biomass and for biochar. The proximate analysis determines the volatile elements, fixed carbon, ashes and moisture content. The ultimate analysis establishes the elemental constituents: C, H, N, S and O (MCLAUGHLIN et al. 2009). Through the results obtained by proximate and ultimate analysis, it is possible to monitor the quantities of these elements at different pyrolysis temperatures and related it to the char yield (TRIPATHI; SAHU; GANESAN, 2016)

Thermogravimetric analysis (TGA) provides the study of thermal decomposition of the biomass used for biochar production. Thus, the TGA curves represent the different stages of degradation of cellulose, hemicellulose and lignin along the heating temperature (REZA et al., 2019). Thermal decomposition of a lignocellulosic material occurs for hemicellulose in a range of 200 °C to 260 °C, cellulose at 240°C to 350 °C and lignin at 280 °C to 500 °C (SJOSTROM, 1993 apud DOWNIE; CROSKY; MUNROE, 2009). Yang et al. (2007) studied the thermal decomposition of pure material of hemicellulose, cellulose and lignin separated. The experiments resulted in decomposition start in ranges of 220 °C to 315 °C for hemicellulose and 315 °C to 400 °C for cellulose. Lignin has a slower process of degradation and the temperature range is from 200 °C to 900 °C.

The X-ray diffraction (XRD), Fourier Transform Infrared Spectrometer (FTIR), Scanning Electron Microscope (SEM) are used to better analyze the biomass (PEREIRA et al., 2016, TALLARICO DA SILVA, 2012). The X-ray diffraction allows to identify the crystalline and/or amorphous phases the material. The distinction of these phases may be important for predicting the stability of the biochar when applied to soils (SINGH; RAVEN, 2017). FTIR is used to find the functional groups of the samples (MANYA, 2012). In different conditions of pyrolysis, the spectra enable to analyze the gradual loss of lignocellulosic functional groups (BREWER et al., 2009).

SEM shows the morphology surface, describing better the physical structure, allowing to detect details about pore structure. And, it makes possible to follow the changes during pyrolysis (AZARGOHAR et al., 2014; DAY et al., 2005; ÖZÇIMEN; ERSOY-MERIÇBOYU, 2010). The IUPAC Manual for physisorption classifies the pores width in macropores (> 50 nm), mesopores (2 nm – 50 nm) and micropores (< 2 nm) (SING et al., 1985). In addition to SEM, other techniques can quantify porosity and pore size distribution. Each technique is

limited to determining specific pore sizes. Analytical methods by radiation such as SEM have a range for mesopores and macropores, while fluid type methods such as gas adsorption ($N_2$ and $CO_2$) detect micropores and mesopores. (ANOVITZ; COLE, 2015).

Another property of the biochar is the water holding capacity (WHC). WHC is related to an interaction between water and biochar. The WHC depends on porosity and bulk volume of biochar and the hydrophobicity (WEBER; QUICKER, 2018). Hydrophobic is the definition of surfaces that repel water and hydrophilic is those surfaces that attract water (LAG et al., 2008). During the pyrolysis process, the biomass becomes more aromatic, because of the decreasing of functional groups, turning its affinity to water lower. The labile compounds with aliphatic surface functional groups in biochar influence the hydrophobicity property (ZORNOZA et al., 2016).

### 1.6.2. Carbon sequester

Plants capture the carbon, nitrogen and other nutrients from air and soil, then they can transform and redistribute these elements through respiration, decomposition, soil organic matter and combustion (SMITH et al., 2014). Biological carbon sequestration is made by soils, dead organic matter and during plants growing. Depending on management of lands or the land use change, carbon can be released or sequestered (EPA, 2019). Biochar has capacity to store the carbon for a sufficiently long time due to its strong resistance to biological decomposition in soil.

### 1.6.3. Climate change and use of biochar

Climate change can naturally occur in a time scale, but this climate change also can be affected by other external forcing, such as human activities. The Industrial Revolution started in large scale emission of greenhouse gases (GHG) from combustion of fossil fuels (coal and oil) (BAEDE et al., 2001).

To assist in the measurement of global warming potential (GWP), a factor to equalize the range of greenhouse gases is defined and updated according to the global emission data. GWP "is an index measuring the radiative forcing following an emission of a unit mass of a given substance, accumulated over a time horizon, relative to CO2". GWP is calculated according to the lifetime of each GHG and over a time horizon that can be a projection for 20, 100 or 500 years (IPCC, 2014).

The index of 100 years for $CO_2$, $CH_4$ and $N_2O$, respectively is 1; 28; 265, as reported in the Fifth Assessment Report (AR5). Fig. 2 shows the contributions by sectors calculated using 100-year GWP. Agriculture, forestry and other land uses activities (AFOLU) represent a quarter of global GHG emissions (IPCC, 2014). Last available data presents AFOLU with 24% of the total emissions, where c.a. 10–12 GtCO2-eq are released per year, mainly caused by deforestation and agricultural emissions from livestock, soil and nutrient management (SMITH et al., 2014).

Figure 2. Contributions by sector to total metric-weighted global GHG emissions in the year 2010, calculated using 100-year GWP.
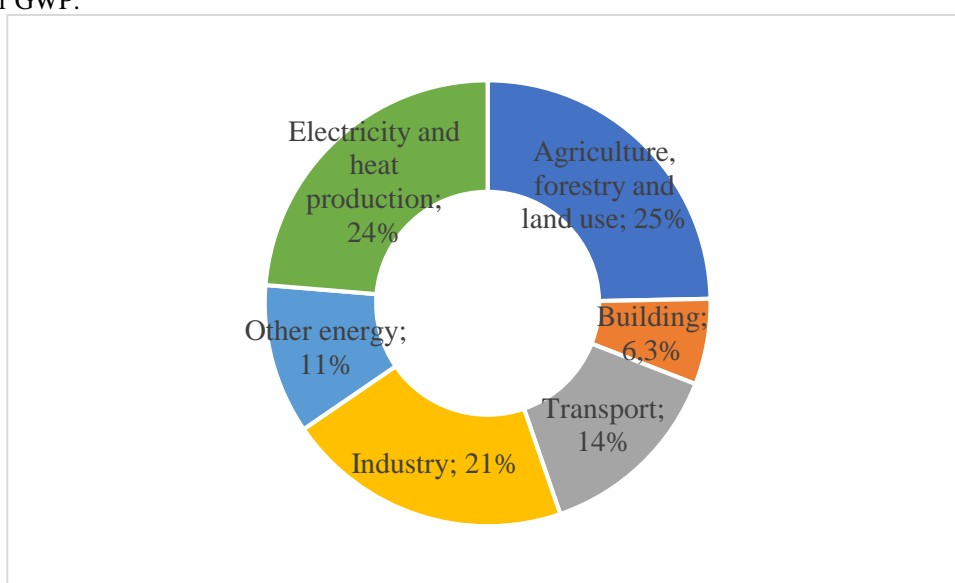


Source: IPCC (2014).

The anthropogenic GHG emission for agriculture and forestry sectors came from: emissions from enteric fermentation; manure management; rice cultivation; synthetic fertilizers; manure applied to soils; manure left on pasture; crop residues; burning crop residues, savanna and cultivation of organic soils; emissions from the net conversion of forest; cropland; grassland and burning biomass for agriculture or other uses (RITCHIE; ROSER, 2017).

The Paris Agreement of the United Nations Framework Convention on Climate Change (UNFCC) limited global warming at 1.5 to 2.0 °C above the pre-industrial level (SMITH et al., 2014). The scenario of the model of $NO_2$ and $CH_4$ emissions, provided by Gernaat et al. (2015) concluded that agricultural sectors will generate the less reduction emission for this century. Thus, the purposes or alternatives of reducing of GHG emissions of agricultural sector is one of the most promising strategies to reach the Paris Agreement goal (WOLLENBERG et al., 2016).

Biochar application is cited as a potential mitigation for GHG emission (GUO et al., 2020; JI et al., 2020; PUGA et al., 2020; SMITH et al., 2014). According to Smith (2016), biochar has a negative emission potential of 0.7 GtCeq $yr^{-1}$ and presents lower impacts beyond others negative emissions technologies. The purpose for the application of biochar in the soil it is because it works as a carbon sequester. The carbon that would be released by natural degradation, remains in the soil in a more stable form than as organic matter. This stability of the biochar is due to its aromatic/chemical structure and recalcitrant nature (MANGRICH; MAIA; NOVOTNY, 2011; PETTER; MADARI, 2012).

## 1.7. BIOCHAR APPLICATION TO SOIL

The addition of biochar in soil can promote changes in physical and chemical properties of the soil (TOMCZYK; SOKOLOWSKA; BOGUTA, 2020; ZHANG, Q. et al., 2020). Physical properties such as soil texture, structure, pore distribution and density impact in water holding capacity (WHC), plant growing, soil aeration (VERHEIJEN et al., 2010).

### 1.7.1. Physical changes

Incorporation of biochar increases porosity improving soil aeration, structure and the growth of roots (TAN et al., 2017) and reduces soil tensile strength (YU et al. 2019). However, depending on the mechanical strength of the biochar, the bulk density can increase (low strength – finer particles) or decrease (high strength) (VERHEIJEN et al., 2010).

The soil retention capacity can imply direct and indirect effects depending on the interaction with biochar. This property is affected by soil texture (particle size), structure (aggregation) and soil organic matter (SOM) content (GLASER; LEHMANN; ZECH, 2002; TOMCZYK; SOKOLOWSKA; BOGUTA, 2020; VERHEIJEN et al. 2010). The biochar pore and particle size and how these features impact bacterial adsorption may contributed to the crop yield increase (BLATT-JANMAAT et al., 2020; ZHANG, L. et al., 2020).

### 1.7.2. Chemical changes

Chemical properties of the soil that are altered by biochar is Cation Exchange Capacity (CEC) and pH (TOMCZYK; SOKOLOWSKA; BOGUTA, 2020; VERHEIJEN et al., 2010). Biochar incorporate to soils can reduce its acidity through its alkaline character, high pH

buffering capacity, its functional group effects and Si effects (YU et al., 2019). Also, fertility can be improved due to biochar composition, such as organic C and other elements (N, P, K, Ca, Mg, S, Fe, Cu, Zn, Si) (DING et al., 2016; YU et al., 2019).

Pot experiment for green waste biochar with radish resulted in significant improvement of the soil, because it was observed an increase in pH, organic carbon and CEC. The reduction of tensile strength occurred in application rates over 50 t ha$^{-1}$ (CHAN et al., 2007). Soil fertility and nutrient availability were enhanced by using Eucalyptus wood biochar (450 °C pyrolysis temperature) in Brazilian savannah (NOVOTNY et al., 2015).

### 1.7.3. Crop effect

According to Van Zwieten et al. (2010) positive or negative effect of biochar (in soil) for crop yield is defined by biochar feedstock and pyrolysis process, soil type and plant species. Review research of Palansooriya et al. (2019) presented a compiled of studies that had biochar application rate varying from 0.1 to 67.5 t ha$^{-1}$ resulting in an increase of crop yield of 2% to 143% over control treatment.

A study using only green waste biochar applied to hard setting soil did not present a significant result for radish dry matter yield for all application rates (0, 10, 50 and 100 t ha$^{-1}$). On the other hand, the increase of radish dry matter yield indicated that biochar applied with N fertilizer had a significant interaction between them (CHAN et al., 2007).

In general, biochar can provide nutrients for sandy soils that are less fertile, while for clay soils that are more fertile, biochar performs better with N availability, mainly in no-tillage and crop rotation systems (NOVOTNY et al., 2005).

Nelissen et al. (2015) studied the effects of woody biochar in spring barley crop by c.a. 2 years. Although the biochar improved some physical properties of the soil after the first application, it was not possible to identify a significant increase in crop yield. This response may be related to an optimum soil fertility condition or due to the biochar failure to reply the drought situation.

According to Jones et al. (2012), the biochar present in barley fields did not affect significantly the crop yield. This means that no negative impacts were observed, so the authors suggest keep the fertilizer, even with the use of biochar.

Obtaining a biochar that achieves the desired objectives requires that the elemental composition and the surface property of the feedstock be previously studied, and the pyrolysis

conditions must also be considered (EL-NAGGAR et al., 2019; TOMCZYK; SOKOLOWSKA; BOGUTA, 2020).

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## CHAPTER 2 - SUGARCANE TRASH BIOCHAR CHARACTERIZATION

**Abstract:** Availability of residues from the sugarcane harvest such as straw or trash requires a better destination for its use. Thus, the objective of this work was the characterization of sugarcane trash biochar produced in different conditions. The biochar was produced in a muffle furnace through slow pyrolysis at three temperatures (200 °C, 325 °C and 450 °C) and two different residence times (2h and 4h). The characterization of the biochar was performed using proximate analysis, pH, thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction, porosity and water drop penetration time (WDPT) test. The factor pyrolysis temperature influenced more than the residence time for the biochar tested. Based on the results, two groups were identified, one was the *in natura* and 200 °C treatments and the other was the 325 and 450 °C treatments. Results indicates that the division occurred because around 315 °C the cellulose starts to decompose, and significative changes happens at this point. Considering the energy use and time to produce biochar, the best condition was 325 °C with 2h residence time.

## 2.1. INTRODUCTION

Brazil is the major producer of sugarcane in the world. Sugarcane planted area to be harvested in Brazilian season is around 8.48 million ha. The 2019/2020 harvest season is estimated in 642.7 million ton (CONAB, 2019). During the harvest and the production of sugar and ethanol, this crop generates around 2/3 of residues, called straw (trash) and bagasse (HASSUANI; LEAL; MACEDO, 2005). All the bagasse is already used in sugarcane mills for energy co-generation (LEAL et al., 2013) and in small scale for second generation ethanol (2G ethanol) (DIAS et al., 2011; ROSA; GARCIA, 2009; PACHECO, 2011). The straw has some issues in how the farmers can use this material.

Sugarcane generates around 14 t ha$^{-1}$ of trash (HASSUANI; LEAL; MACEDO, 2005). Some authors indicate that the trash could remain on the field for covering the land and preventing from erosion, weeds and leaching (SILVA et al., 2012). On the other hand, this process can attract some insects that damage the crop and generate economic losses (MANECHINI; RICCI JÚNIOR; DONZELLI, 2005). One way to aggregate value to this residue could be recover part of this trash and give it another purpose (CARVALHO et al., 2016).

Difficulties during the use of sugarcane trash for energy production, is caused by high amount of soil impurities and silica (NAKASHIMA et al., 2017). However, its use as soil amendment could be an alternative because this undesirable items for energy is not a problem for soil application. Therefore, biochar is one type of charcoal that presents features for soil improvement (SKJEMSTAD et al., 1999). Biochar is defined by Friedman, Treadwell and Wilkie (2012) as a "solid by-product of organic matter that has been heated in a closed container with little or no available oxygen".

Biochar has great characteristics as high CEC (JEONG; DODLA; WANG, 2016; LIANG et al. 2006; TOMCZYK; SOKOLOWSKA; BOGUTA, 2020), pore volume (JEONG; DODLA; WANG, 2016; SONG; GUO, 2012; BREWER et al., 2014), higher water holding capacity (JEONG; DODLA; WANG, 2016).These features enable the uses for biochar to energy (MCHENRY, 2009; WAQAS et al., 2018), soil amendment (CHA et al., 2016; JEONG; DODLA; WANG, 2016; SINGH; SINGH; COWIE, 2010), carbon sequestration (JEONG; DODLA; WANG, 2016; MATOVIC, 2011), improvement of nutrient dynamics (JEONG; DODLA; WANG, 2016), adsorption (CHA et al., 2016; WAQAS et al., 2018).

Brewer et al. (2014) observed that some characteristics are controlled by pyrolysis conditions and some others are controlled by biomass anatomy (feedstock). The parameters (temperature, residence time, feedstock) combined with the characterization of the product are very important to find the final use for the biochar. According Pires et al. (2018), the best pyrolysis condition to produce sugarcane trash biochar was 3 hours residence time at 250 °C. Then, the aim of this study was to determine the best slow pyrolysis conditions for sugarcane trash biochar. For this purpose, a physicochemical characterization was realized for the produced biochar.

## 2.2. MATERIAL AND METHODS

### 2.2.1. Material

Sugarcane (*Saccharum officinarum* L.) trash was collected at Corredeira Farm, located in Ibaté, São Paulo State, Brazil. The farm has 800 ha of planted area with an average yield of 87 t ha$^{-1}$. The sugarcane varieties planted on the farm are RB 855453, RB 867515, RB 855536, SP 803280, SP 813250. Sugarcane trash was dried in an oven at 105 °C and crushed into 50 mm pieces.

### 2.2.2. Biochar Production

Crucibles and lids were used to settle the sugarcane trash samples. The higher amount (around 18 g) of sugarcane trash was added to the crucible to avoid the $O_2$ concentration. It was used a muffle furnace Jung model 0212. Conditions for the biochar production were fixed based on previous study by Pires et al. (2018) and Trugilho et al. (2001). Biochar production was performed in three different pyrolysis temperatures (200 °C, 325 °C, 450 °C) and two residence time (2h and 4h) in the muffle furnace.  The treatments were: 200_2 (200 ℃ / 2h); 200_4 (200 ℃ / 4h); 325_2 (325 ℃ / 2h); 325_4 (325 ℃ / 4h); 450_2 (450 ℃ / 2h) and 450_4 (450 ℃ / 4h).

### 2.2.3. Gravimetric yield and proximate analysis

Gravimetric yield of biochar was obtained according to Róz et al. (2015), in triplicate, described in the equation 1:

$$Y = (m_1/m_2) \times 100 \hspace{3cm} (1)$$

where, $Y$ = Gravimetric yield of biochar production (%); $m_1$ = Biochar mass (g); $m_2$ = Dry mass before pyrolysis (g).

Proximate analysis was done based on ASTM 1762 standard. Previously, porcelain crucibles and lids were calcined in muffle at 750 °C for 20 min. Sample was dried in an oven at 105 °C for 2h. Crucibles, lids and sample were cool in a desiccator and weight. Three replicates were performed, with 1.0 g of biochar added to each crucible. With the crucible covered, the system was placed in the muffle with the door open at 950 °C for 3 minutes and with the door closed for 6 minutes for volatile matter (VM). After analysis, the samples were cooled in a desiccator for 1h and weighed. For the quantification of the ash content (AC), the crucible without cover with the residual sample of the volatiles is placed in the muffle at 750 °C. After 6h, the system is cooled in a desiccator and weighed. Fixed carbon (FC) was calculated by difference (%FC = 100% - %VM – %AC – %Moisture content).

### 2.2.4. pH

The pH was determined based on JIS K-1474-1992 Standard with microprocessed digital pHmeter (PG1800 - Gehaca) in triplicate. In a 250 mL-Erlenmeyer flask was added the biochar samples (1.0 g) and 100 mL of distilled water. The flasks were placed on a hot plate

until boiling for 5 minutes. After cooling, another 100 mL of distilled water was added to measure the pH with a pH meter.

### 2.2.5. Thermogravimetric analysis (TGA)

Samples were cut in small pieces (2.0 mm) and about 1.5 mg were used for each treatment. TG analysis was done in TG/DTA 6200-Exstar 6000 series, Seiko instruments and Muse Jobs software in Structural Materials Research Institute at National Institute of Advanced Industrial Science and Technology (AIST- Nagoya, Japan). TGA was conducted under synthetic air with flow rate of 100 ml min$^{-1}$ and heating rate of 7 °C min$^{-1}$ from room temperature to 600 °C.

### 2.2.6. Fourier transform infrared spectroscopy (FTIR)

The functional groups were characterized by Thermo Scientific (FTIR-ATR), Nicolet 8700 and OMNIC software in Structural Materials Research Institute at National Institute of Advanced Industrial Science and Technology (AIST- Nagoya, Japan).

### 2.2.7. X-Ray diffraction (XRD)

The X-ray diffraction was recorded with Rigaku, Ultima IV diffractometer, with scanning range of 2θ : 5° to 45° and speed of 3° min$^{-1}$, with voltage of 40 kV and current of 40 mA. For treatment *in natura*, 200_2 and 200_4, 325_2, 325_4, 3 tablets were prepared. For treatments at 450 °C (450_2, 450_4) treatments, the powder was compressed on a glass sample holder, because of the difficulty in tablet formation. The analysis was done in Nagoya University, Nagoya, Japan.

Other analysis was for XRD was determined in an equipment Shimadzu model LABX XDR-6100 in the Physics Laboratory, at Federal University of São Carlos, Sorocaba, SP, Brazil. The powdered biochar was placed on the glass holder to obtain the diffractograms. The scan range was 2θ : 5° to 45° on the diffractometer with a monochromatic CuKα radiation (λ = 1.5406 Å), voltage of 40 kV and current of 30 mA and speed scanning of 2° min$^{-1}$. In order to verify the difference between 2h and 4h residence time, a furnace coupled to XRD equipment was used. The sample of sugarcane trash *in natura* was analyzed using a special sample holder

(alumina composition) and was submitted until a temperature of 200 °C. The scanning was done after 2h, 3h and 4h residence time.

### 2.2.8. Porosity

Porosity is "the fraction of void volume over total volume" (ANOVITZ; COLE, 2015). Porosity measurement was analyzed by 2 different techniques: porosity adsorption (micropores) and scanning electron microscopy – SEM (macropores), both analyses were done in Structural Materials Research Institute at National Institute of Advanced Industrial Science and Technology (AIST- Nagoya, Japan). Samples of sugarcane trash *in natura,* 200_2, 200_4, 325_2, 325_4, 450_2 and 450_4 were submitted to porosity adsorption and SEM analysis.

Porosity adsorption was evaluated using automatic gas adsorption device, Quantachrome Autosorb-1, with $CO_2$ described by Nakatani et al. (2008). Approximately 0.5 g of biochar in 2 mm particle sizes were used for each measurement. Vacuum outgassing was performed as a pre-treatment in different conditions for each biochar temperature. The pore size distribution of micropores was determined using HK method (HORVÁTH; KAWAZOE, 1973).

Scanning Electron Microscopy (JEOL/EO – JSM 5000) was used to analyze the biochar samples. Biochar samples were dried at 105 °C and a sputter coating technique was used before the analysis.

### 2.2.9. Hydrophobicity

The hydrophobicity of the produced biochar was tested through the water drop penetration time (WDPT) test. The method measures the necessary time for 1 drop to infiltrate the biochar surface, according to Bisdom, Dekker and Schout (1993). It was used a goniometer (100-25M - Ramé-Hart), Fig. 3, located at Physics Laboratory at Federal University of São Carlos, Sorocaba, SP, Brazil. The classification used to characterize the hydrophobicity of the biochar was: hydrophilic (< 5s); slightly hydrophobic (6-60s); strongly hydrophobic (61-600s); severely hydrophobic (601 – 3600s); extremely hydrophobic (> 3600s) (BISDOM; DEKKER; SCHOUT, 1993; SATO et al., 2019).

Figure 3. Goniometer equipment (left) and the sample-holder with biochar and water drop (right).
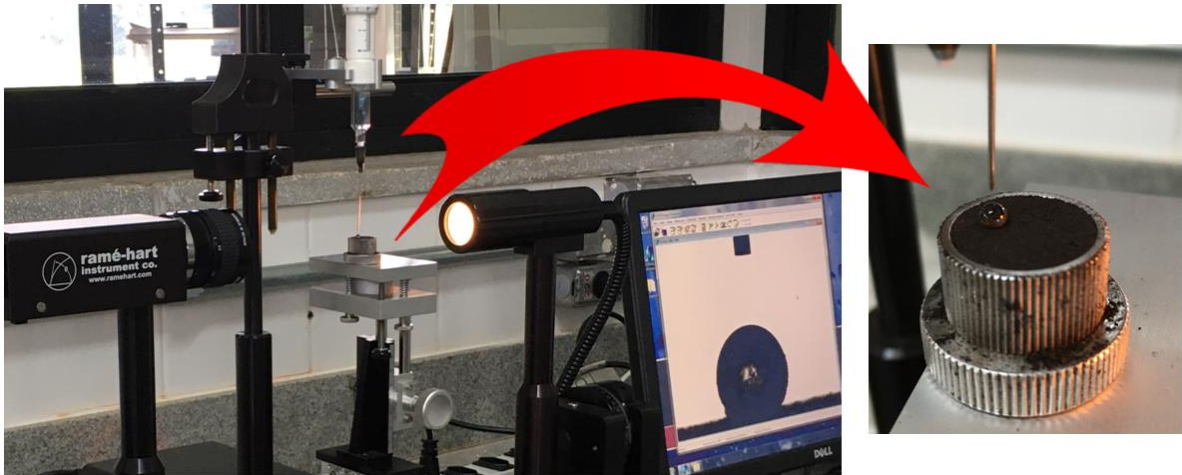


## 2.2.10. Statistical Analysis

The data from proximate analysis and pH values were analyzed by one-way ANOVA ($p < 0.05$) and Tukey HSD (honestly significant difference) test, using R software.

## 2.3. RESULTS AND DISCUSSION

### 2.3.1. Biochar production

Fig. 4 has the different results of the carbonization of sugarcane trash biomass.

Figure 4. Biochar produced by different conditions: 200 °C/2h, 200 °C/4h, 325 °C/2h, 325 °C/4h, 450 °C/2h and 450°C/4h.

Fig. 4 shows difference between the pyrolysis temperature conditions. Although, it is not possible to verify the visual difference for residence time. Biochar 200 °C presented higher number of pieces with 10 mm or more and did not present the dark black color like other treatments. The change in color was also observed by Berthet et al., (2016) and Li et al. (2018). The authors that studied biomass from corncob reported that the increasing in temperature from 220 °C to 300 °C caused the darkening of the torrefied corncobs (LI et al., 2018).

### 2.3.2. Basic characteristics

Proximate analysis and gravimetric yield are presented in Table 2.

Table 2. Proximate analysis, biochar yield and pH mean for biochar and *in natura* samples.

| Treat. | Volatile matter (%) | | Ash content (%) | | Fixed carbon* (%) | | Biochar yield (%) | | pH | |
|---|---|---|---|---|---|---|---|---|---|---|
| *in natura* | 76.3[a] | (0.33) | 7.1[a] | (0.36) | 16.5[a] | (0.14) | - | - | - | - |
| 200_2 | 76.0[a] | (0.85) | 5.3[a] | (0.25) | 18.6[a] | (0.81) | 92.5 | (1.19) | 5.57[a] | (0.22) |
| 325_2 | 31.1[b] | (0.06) | 17.4[b] | (0.68) | 51.4[b] | (0.71) | 30.6 | (0.79) | 7.18[b] | (0.15) |
| 450_2 | 18.9[d] | (0.78) | 20.8[c] | (0.26) | 60.1[d] | (1.03) | 27.8 | (0.00) | 8.72[c] | (0.04) |
| 200_4 | 75.6[a] | (0.24) | 6.3[a] | (0.11) | 18.0[a] | (0.21) | 90.9 | (0.04) | 5.40[a] | (0.16) |
| 325_4 | 31.6[b] | (0.79) | 15.7[b] | (0.68) | 52.6[b] | (0.85) | 33.0 | (1.10) | 7.06[b] | (0.33) |
| 450_4 | 13.4[c] | (0.61) | 30.4[d] | (1.61) | 56.2[c] | (1.17) | 22.4 | (0.00) | 8.77[c] | (0.08) |

Number inside parenthesis represents the standard deviation of each mean.
Different lowercase letter in a column indicates difference between treatments ($p < 0.05$).
* result for fixed carbon was obtained by mass difference.

Table 2 shows that gravimetric yield and fixed carbon are inversely proportional also noted by Okimori, Ogawa and Takahashi (2003). In general, yield tends to be lower with increasing the pyrolysis temperature (DEMIRBAS, 2009; OKIMORI; OGAWA; TAKAHASHI., 2003; SONG; GUO, 2012; RÓZ et al., 2015).

The results for proximate analysis showed statistically difference for pyrolysis temperature. These indicate that biochar produced will present different properties. The 200 °C treatments and *in natura* did not present the significative differences at 5% level, by Tukey HSD Test. This result indicates that temperature (200 °C) was not enough to present significative changes. The residence time (2h and 4h) showed significative difference (volatile, ash and fixed carbon) for 450 °C.

During the pyrolysis, the product loses a percentage of volatiles, consequently the amount of ash content, fixed carbon increase, as expected. For this study, both residence times

presented an increase of 3 times for fixed carbon values with the increase of pyrolysis temperature, from 200 °C to 450 °C.

The ashes (from 200 °C to 450 °C) was increased by 292% for 2h and 382% for 4h. These results are related to biochar yield. The amount of mineral parts did not change but biochar yield is lower for high temperatures. This trend was also noted by Jeong, Dodla and Wang (2016), where the ashes had an increase by 29.5% for biochar sugarcane leaves from 450 °C to 750 °C pyrolysis temperature.

Volatile matter had a decrease from 76.3% (*in natura*) to 18.9% (450_2) and 13.4% (450_4). Volatiles is still found on all biochar treatments because the incomplete thermal degradation (ÖZÇIMEN, ERSOY-MERIÇBOYU, 2010). Manya (2012) reported that high percentages of volatile matter in biochar might decrease their quality for soil application. A study realized with charcoals containing high volatile matter (22.5%) followed in negative responses for corn development (DEENIK et al., 2010). The loss of volatiles, during the carbonization, is related to the decrease of O/C and H/C atomic ratios, increasing the carbon concentration and aromatic structures in biochar (WINDEATT et al., 2014)

Brazilian soils are, in general, from medium to high acidity ($pH_{H2O} > 5$), causing low productivity in agriculture (VELOSO et al., 1992). Biochar is normally alkaline and can increase soil pH with increasing application rates (DAI et al., 2017; YU et al., 2019). The pH results were significant different among the pyrolysis temperatures but did not present significant difference for residence time.

Overall, results for pH showed that the raise of pyrolysis temperature, increased the pH values from 5.4 to 8.8 (Table 2). For sugarcane leaves biochar, pH increased from 8.3 to 9.6 of 450 °C to 750 °C pyrolysis temperatures, respectively (JEONG; DODLA; YANG, 2016). Similar result was also shared by Yuan, Xu and Zhang (2011), who concludes that all biochar produced by them had a basic character and the alkalinity of the biochar was increased according to the increase in the pyrolysis temperature. This behavior can be explained by the influence that at higher temperatures, the material loses organic functional groups and increases its inorganic fraction (JEONG; DODLA; WANG, 2016), such as $SIO_2$, $CaO$, $Fe_2O_3$ and $Al_2O_3$ for sugarcane straw (NAKASHIMA et al., 2017), influencing the increase in pH. Considering the pH values for the different residence times, the difference is not significant at the 5% level. The basic characteristic of biochar is beneficial for Brazilian acidic soils.

### 2.3.3. Thermogravimetric Analysis (TGA)

The Thermogravimetric Analysis (TGA) and the Difference Thermogravimetric (DTG) Analysis of sugarcane trash *in natura* and biochar performed in an oxidizing atmosphere are shown in the Fig. 5 and Fig. 6. The data for Tonset and Toffset, Tmaximum and the respective mass losses per degradation stage are shown in the Table 3.

Figure 5. Thermogravimetric (TG) and Derivative Thermogravimetric (DTG) curves for each treatment: (a) TG curves and (b) DTG curves for 2h residence time; (c) TG curves and (d) DTG curves for 4h residence time.
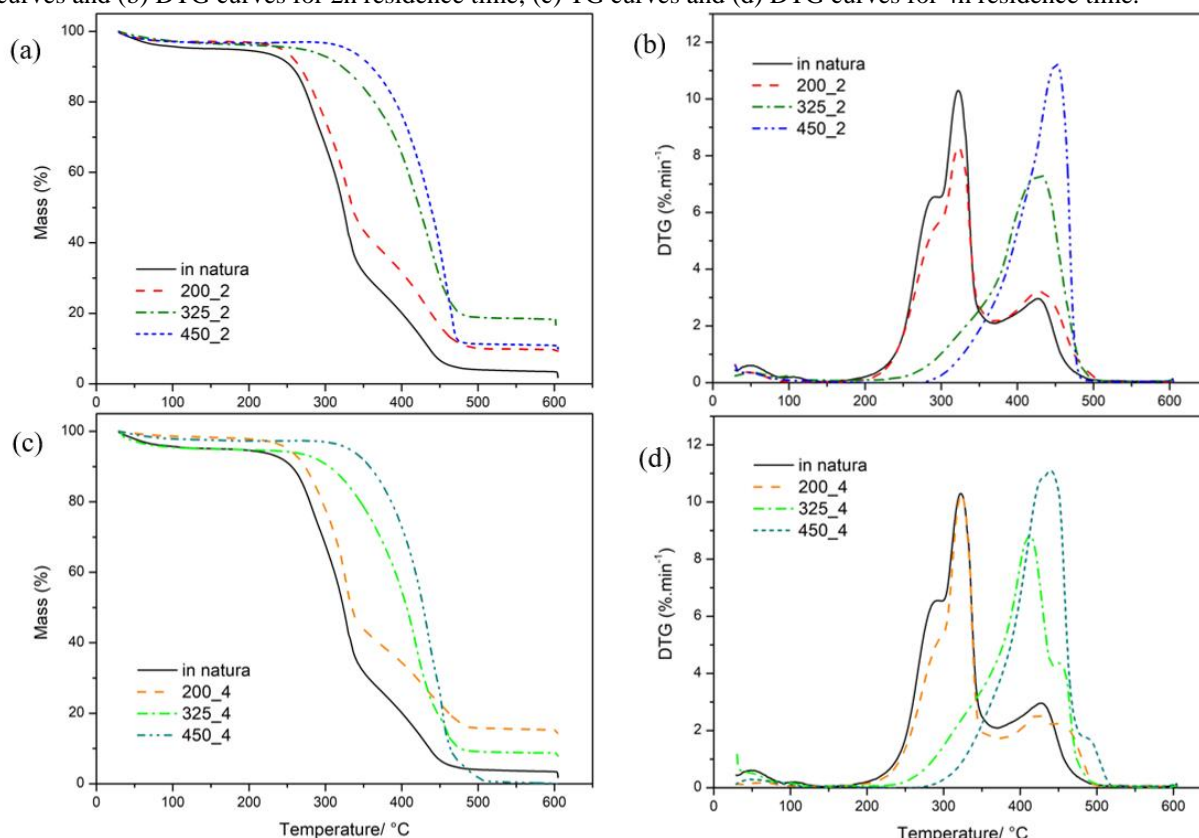


Through the curves obtained by TG and DTG it is possible to identify 3 stages of degradation for the *in natura* material (REZA et al., 2019) and for the biochar treatments produced at 200 °C. For treatments 325_2, 325_4, 450_2 and 450_4 only 2 stages are identified.

For all treatments, the first event happened to release the moisture from the samples. The second stage observed for *in natura* material and biochar at 200 °C showed a peak of degradation at 322 °C. This event was preceded by a shoulder on DTG close to a temperature of 275 - 290 °C for these treatments, which can mean the breakdown of hemicellulose (MIMMO et al., 2014). This shoulder is more prominent for *in natura* curves (Fig. 5b and 5d). For biochar at 200 °C, the shoulder is less prominent, indicating that the hemicellulose and cellulose breakdown reactions happen concurrently (YANG et al., 2007).

Table 3. Stages of thermogravimetric analysis (TGA) and Tonset (start temperature), Tmax (temperature of the degradation peak), Toffset (end temperature), Mass loss for each stage.

| Treat. | Stage | Tonset (°C) | Tmax (°C) | Toffset (°C) | Mass loss (%) |
|---|---|---|---|---|---|
| *in natura* | I | 30.0 | - | 70.1 | 5.04 |
| | II | 256.4 | 322.3 | 337.1 | 59.33 |
| | III | 405.7 | 428.6 | 456.3 | 31.04 |
| 200_2 | I | 29.3 | | 72.8 | 2.33 |
| | II | 252.6 | 322.3 | 340.8 | 50.78 |
| | III | 399.5 | 430.4 | 468.5 | 36.06 |
| 325_2 | I | 29.7 | - | 95.3 | 3.26 |
| | II | - | - | - | - |
| | III | 336.2 | 428.0 | 463.5 | 96.47 |
| 450_2 | I | 29.7 | - | 79.0 | 3.26 |
| | II | - | - | - | - |
| | III | 372.3 | 451.4 | 471.9 | 85.24 |
| 200_4 | I | 30.0 | - | 86.9 | 1.17 |
| | II | 254.0 | 322.3 | 339.0 | 50.28 |
| | III | 407.2 | 423.4 | 482.1 | 31.8 |
| 325_4 | I | 30.7 | - | 64.8 | 4.94 |
| | II | - | - | - | - |
| | III | 312.9 | 411.8 | 470.0 | 85.89 |
| 450_4 | I | 29.8 | - | 82.2 | 2.73 |
| | II | - | - | - | - |
| | III | 357.1 | 438.5 | 466.5 | 96.95 |

The biochar produced at higher temperatures such as the 325 °C and 450 °C treatments, performed a one-step curve with broader ranges of degradation (MIMMO et al 2014), and only started their greatest loss of mass after 300 °C. This behavior indicates that there is no presence of hemicellulose. The degradation peak of hemicellulose occurred up to 290 °C for *in natura* and 200 °C biochar. The biochar treatments (325 °C and 450 °C) did not presented the peak of hemicellulose because they were produced in temperatures equal or above 325 °C. The maximum peaks of degradation for these treatments (325 °C and 450 °C) are related to cellulose degradation: 428 °C (325_2), 411 °C (325_4), 451 °C (450_2),438 °C (450_4). The treatments *in natura*, 200_2 and 200_4 also presented a considerable weight loss (related to cellulose) in this temperature range. The peak of degradation for these treatments was 428 °C (*in natura*), 430 °C (200_2) and 423 °C (200_4).

Lignin is more complex and presents different chemical bonds, thus not having a specific range, starting the thermal degradation in 200 °C. Because lignin degradation extends to temperatures like 900 °C (YANG et al., 2007), it is possible that the stage III is due to the thermal degradation of this compound.

Figure 6. Thermogravimetric (TG) and Derivative Thermogravimetric (DTG) curves for: (a) 200 °C pyrolysis temperature with 2 and 4h residence time; (b) 325 °C pyrolysis temperature with 2 and 4h residence time and (c) 450 °C pyrolysis temperature with 2 and 4h residence time.
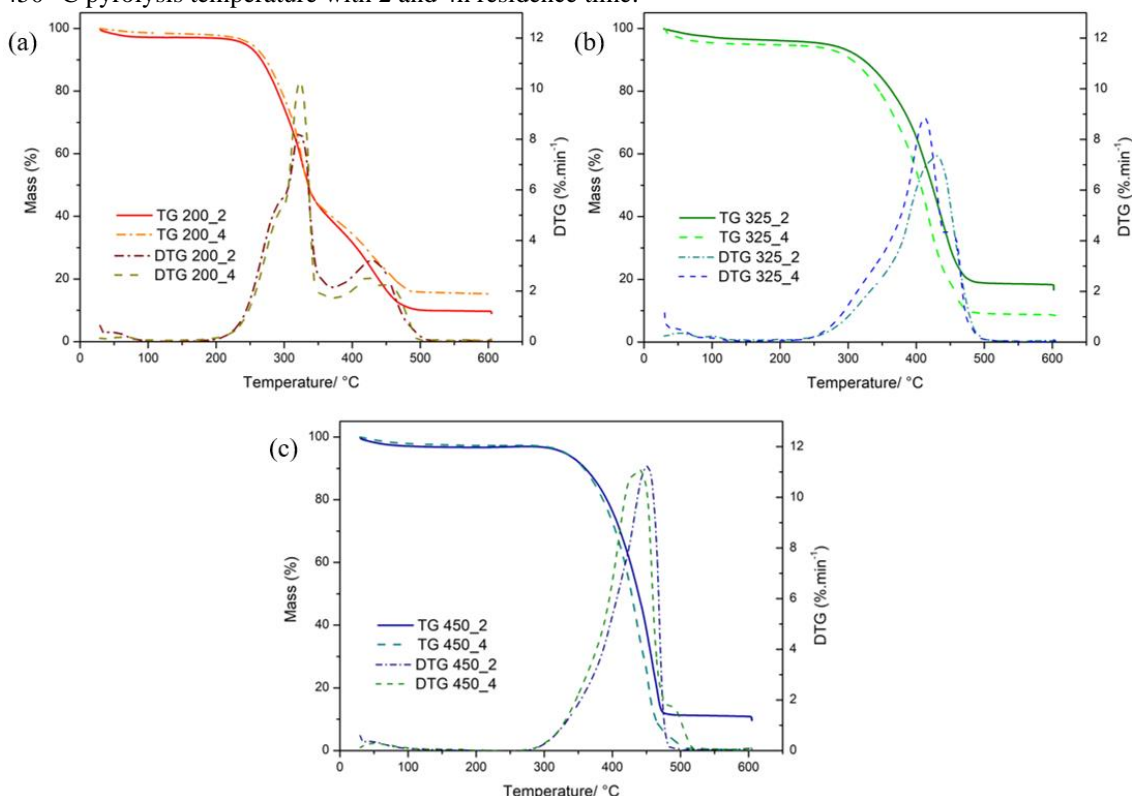


## 2.3.4. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded in ATR (Attenuated total reflection) mode for the sugarcane trash *in natura* and biochar samples. Results from FTIR spectra in Fig. 7 indicate that the difference between 2 and 4h residence time (Fig. 7a and 7b) was just between the intensity of the peaks.

Figure 7. Fourier Transform Infrared spectroscopy spectra of the sugarcane trash *in natura* and biochar, (a) treatments of 2h residence time, (b) treatments of 4h residence time.
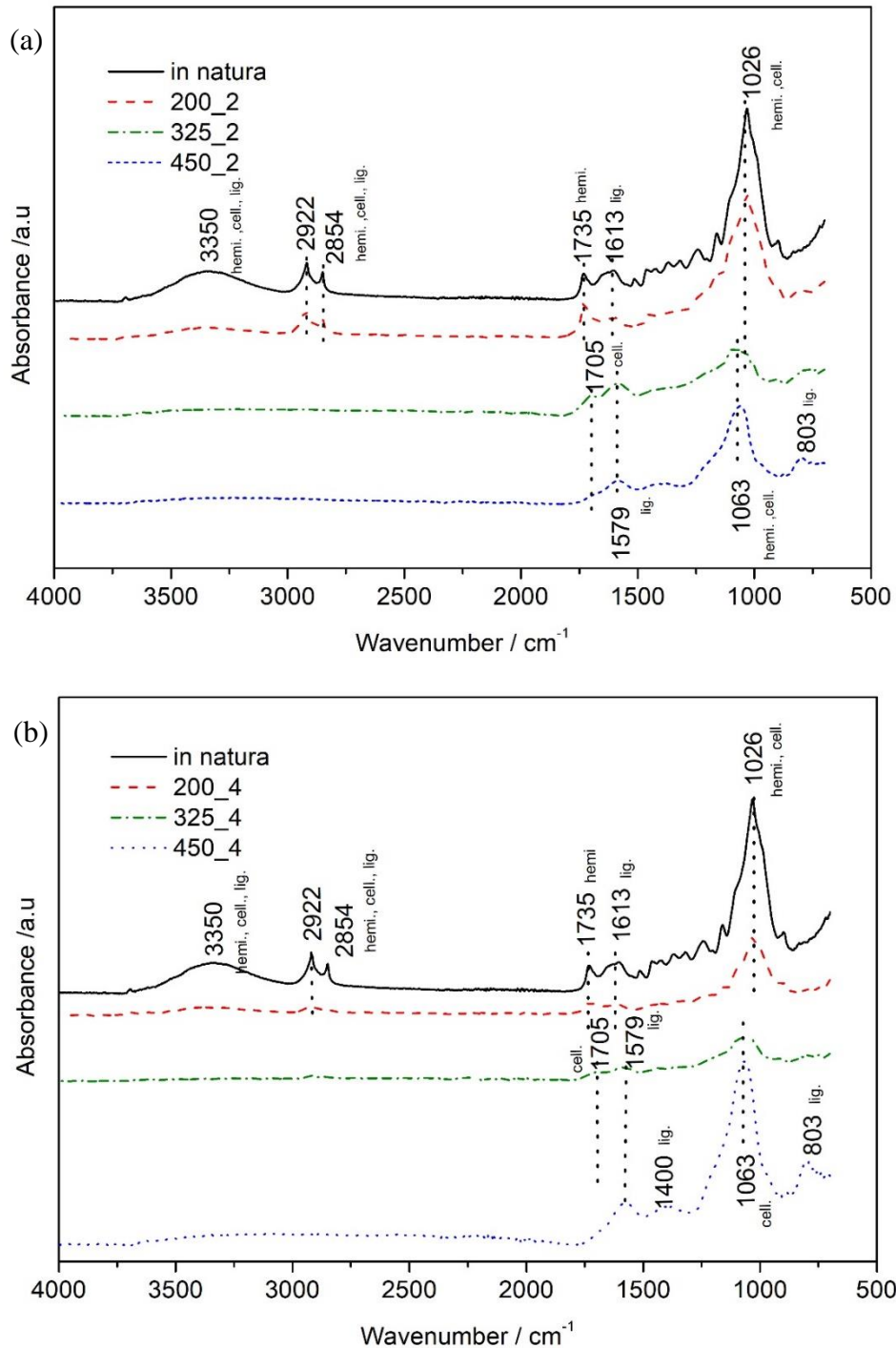


FTIR spectra expose that the pyrolysis transforms the biomass. This transformation is noted when occurs an attenuation of signals. In the curves for *in natura* is observed a signal for O-H stretching bands (3350 cm$^{-1}$). This signal (O-H stretching) is not present in curves 200, 325 and 450 °C because of the dehydration (BREWER et al., 2009; MIMMO et al., 2014) and some volatile functional groups (USMAN et al., 2015). Also, *in natura* curves is observed CH stretching in aliphatic formation (2960 - 2850 cm$^{-1}$), which represents the presence of

hemicellulose, cellulose and lignin in biomass (REZA et al., 2019). This signal remained in spectrum 200_2. In other spectra (200_4 and all spectra 325 °C and 450 °C) there is no CH stretching (2960 - 2850 cm$^{-1}$) indicating the degradation of hemicellulose and cellulose, because, possibly occurred a loss in polar functional groups with increasing of pyrolysis temperature (USMAN et al., 2015)

The higher temperature treatments (biochar 325 °C and 450 °C) of pyrolysis showed an increase in the degree of aromaticity of the product, as seen by the maintenance of aromatic bands described in Table 4.

Table 4. FTIR absorbance bands for sugarcane trash *in natura*, and biochar treatments, according to Kataoka (2000) and Özçimen and Ersoy-Meriçboyu (2010).

| Treatment | Absorption peak wave number (cm$^{-1}$) | Bond assignment |
|---|---|---|
| *in natura* | 3350 | -OH stretching (cellulose, hemicellulose, lignin) |
| | 2922 | Aliphatic CH stretching (cellulose, hemicellulose, lignin) |
| | 2854 | Aliphatic CH stretching (cellulose, hemicellulose, lignin) |
| | 1735 | Aromatic carbonyl/carboxyl C=O stretching (hemicellulose) |
| | 1613 | Aromatic C=C ring stretching (lignin) |
| | 1026 | Aliphatic ether C-O and Alcohol C-O stretching (cellulose, hemicellulose) |
| 200 °C | 2922 | Aliphatic CH stretching (cellulose, hemicellulose, lignin) |
| | 2854 | Aliphatic CH stretching (cellulose, hemicellulose, lignin) |
| | 1735 | Aromatic carbonyl/carboxyl C=O stretching (hemicellulose) |
| | 1613 | Aromatic C=C ring stretching (lignin) |
| | 1026 | Aliphatic ether C-O and Alcohol C-O stretching (cellulose, hemicellulose) |
| 325 °C | 1705 | C-H bending (cellulose) |
| | 1579 | Aromatic C=C ring stretching (lignin) |
| | 1063 | Aliphatic ether C-O and Alcohol C-O stretching (cellulose) |
| 450 °C | 1579 | Aromatic C=C ring stretching (lignin) |
| | 1400 | Aromatic C=C ring stretching (lignin) |
| | 1063 | Aliphatic ether C-O and Alcohol C-O stretching (cellulose) |
| | 803 | Aromatic C-H bending (lignin) |

Peak in the wavenumber of 850 to 780 cm$^{-1}$ was just found in 450_2 and 450_4 biochar and indicates a C-H aromatic bending vibration from lignin (MOHAMMED et al., 2015). The increase in aromatic substances makes the biochar more stable, but this increase is a consequence of the loss of functional groups that can interfere with the decrease in the cation exchange capacity (CEC) of the biochar (MIMMO et al., 2014). However, characteristic peaks of cellulose determined by the wavenumber for 1200 - 1000 cm$^{-1}$ (such as OC stretching) were still detected, even in the 450 °C biochar, a situation that was also observed by Mimmo et al. (2014). This result indicates that possibly some cellulose remains in all treatments.

### 2.3.5. X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a technique to identify the crystallinity of the materials. XRD diffractograms were done as a trial with an X-ray diffractometer Rigaku with scanning speed 2° min$^{-1}$ and 3° min$^{-1}$. The results are shown in Fig 8 (scan speed 3° min$^{-1}$), and in Fig. 9 (scan speed 2° min$^{-1}$).

Figure 8. Diffractogram obtained with 3° min$^{-1}$ of scanning speed for all treatments: (a) *in natura* and 200 °C biochar treatments, (b) *in natura* and 325 °C biochar treatments, (c) *in natura* and 450 °C biochar treatments.
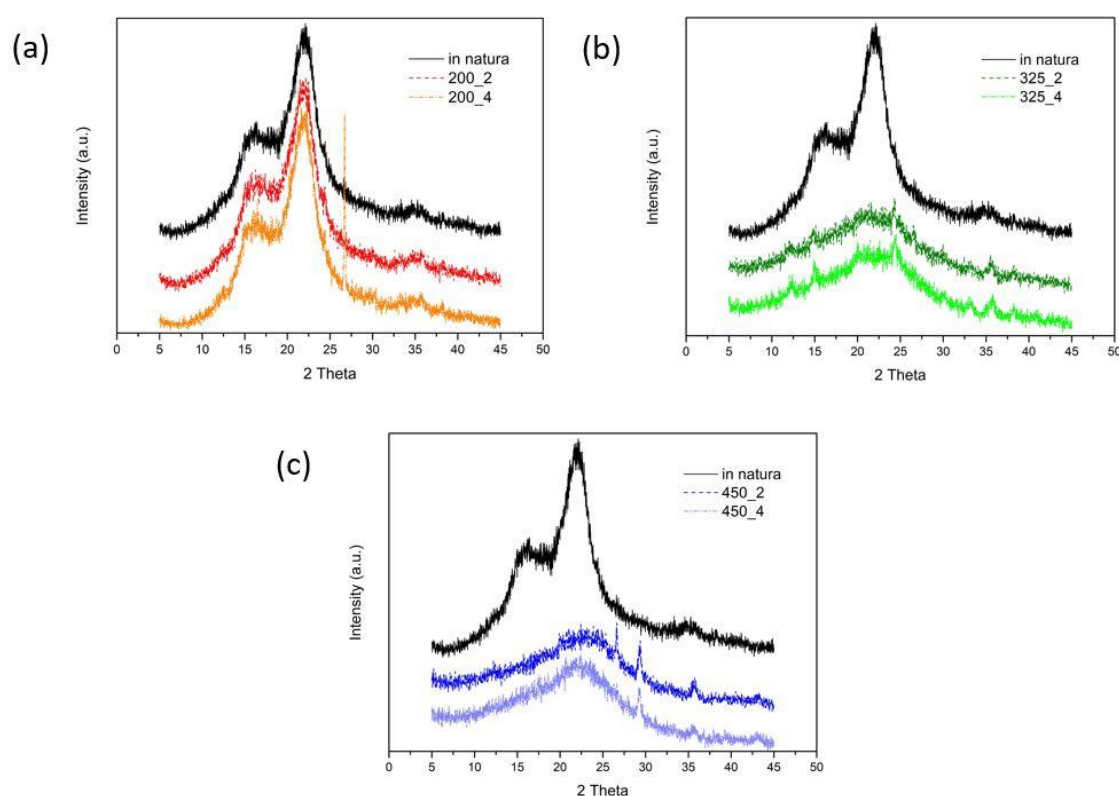


The diffractograms showed that the factor temperature has influence on biochar crystallinity. The noises presented in diffractograms did not allow better results. A second X-

ray diffraction analysis (Fig. 9) was done using x-ray diffractometer Shimadzu XRD-6100. The scanning speed was 2° min$^{-1}$.

Figure 9. X-ray diffraction patterns of sugarcane trash *in natura* and its biochars: (a) diffractograms for all studied samples: *in natura*, biochar 200 °C (200_2 and 200_4), biochar 325 °C (325_2 and 325_4) and biochar 450 °C (450_2 and 450_4); (b) sugarcane trash in natura sample at 200 °C and residence time of 2h, 3h and 4h coupled with a furnace at DRX, Sample Holder (SH) pattern.

(b)
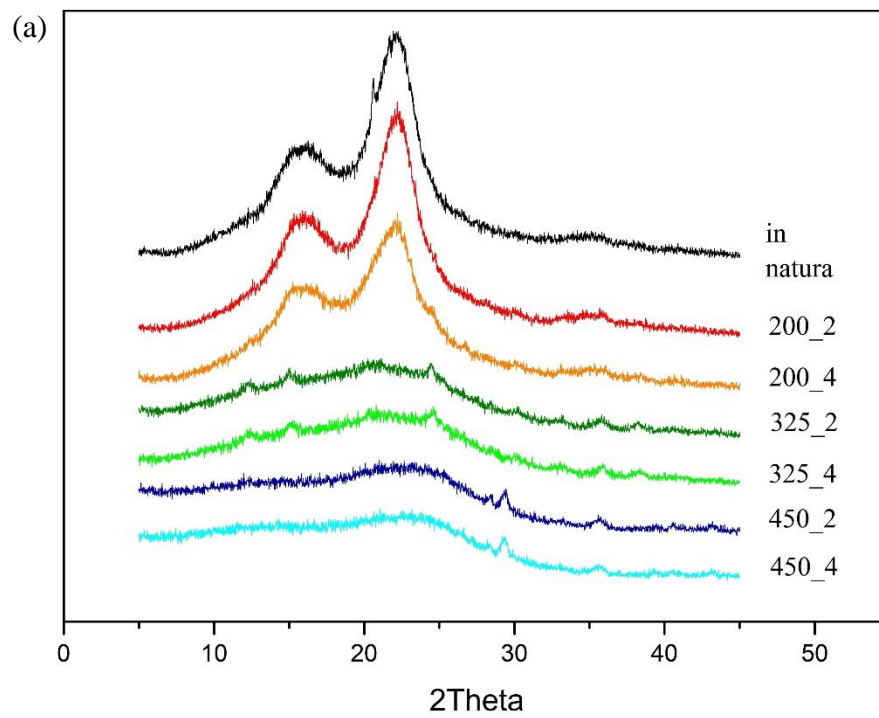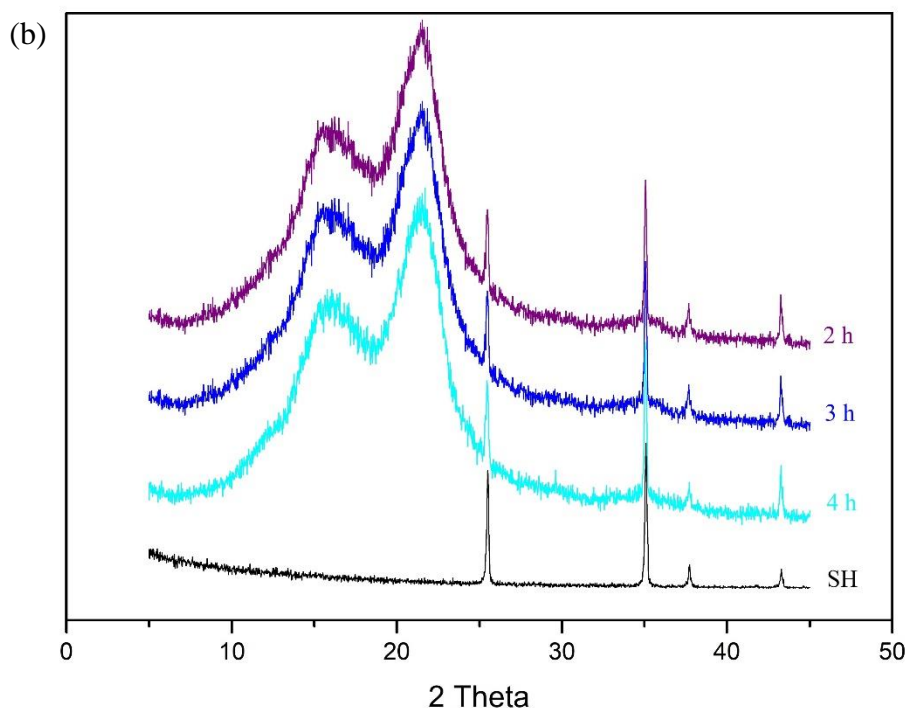


The results showed a crystallinity on the diffractogram (Fig. 9a) for *in natura*, 200_2 and 200_4 biochar is presented by two broad peaks at 16° and 22° 2θ. Shaaban et al. (2013) reported the broad peaks, 16° and 22° for raw and 300 °C biochar of rubber wood sawdust, that might be due to the presence of cellulose, since hemicellulose and lignin have amorphous structures (MOHAMMED et al., 2015). XRD patterns (Fig. 9a) explain the cellulose degradation. The cellulose crystallinity is clearly observed for materials *in natura* and biochar at 200 °C (2h and 4h). The peaks for *in natura* is kept for biochar at 200 °C indicating that cellulose has not been degraded.

Considering that cellulose starts its thermal degradation around 315 °C (YANG et al., 2007), it is observed the biochar treatments from 325 °C (325_2, 325_4) and 450 °C (450_2, 450_4) exhibit a broad hump centered at 23° 2θ, as also described by Prakongkep et al. (2013) and Singh and Raven (2017). These authors attributed this broad hump at ~23° 2θ to the presence of amorphous carbon and possible amorphous silica.

The broad peaks previously detected at 16 ° and 22°, for higher temperatures presented a flattening of these peak at 23°, which indicates less crystallinity showing the cellulose degradation (AZARGOHAR et al., 2014). Similar result was presented in TGA (Fig. 6) and FTIR spectra (Fig 7). Up to 200 °C pyrolysis temperature did not modify the material structure. The degradation is clearly observed for biochar samples at 325 °C and 450 °C.

The sharp and with low intensity peaks identified on biochar 325 °C and 450 °C may be indicated by inorganic material, due to the high amount of ash in sugarcane (HASSUANI; LEAL; MACEDO, 2005; KEILUWEIT et al., 2010).

The XRD data for same temperature (200 °C) and different residence times are displayed in Fig. 9b. Through this result, it was not detected differences between 2, 3 or 4h residence time. The sharp peaks were caused by the influence of the sample holder (SH), that has alumina in its composition. Also considering the results of Fig. 9a, there was a similarity between the diffractograms from same temperature and 2h and 4h residence times, highlighting that the temperature was the main factor for the crystallinity degradation of the cellulose I structure.

### 2.3.6. Porosity

Fig. 10a shows isotherm $CO_2$ adsorption at different residence time and pyrolysis temperatures and Fig. 10b the pore size distribution using the HK method. $CO_2$ adsorption technique to obtain the pore size distribution is mainly used for sub-micropores (ANOVITZ; COLE, 2005).

Figure 10. Graph (a) represents the isotherm from $CO_2$ adsorption at 273 K. (b) The pore size distribution of *in natura* and biochar samples, using HK method.
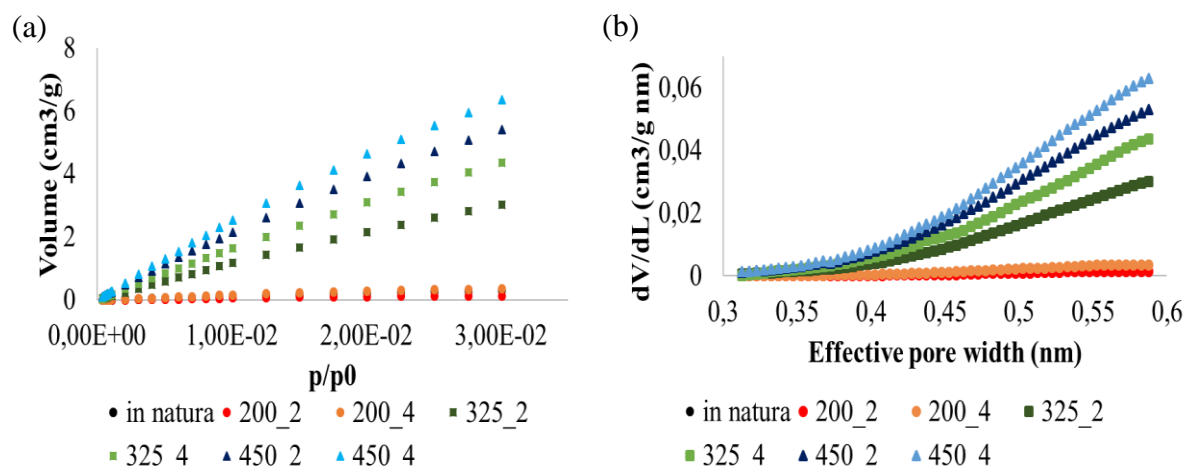


According to the Sing et al. (1985), the isotherm (Fig. 10a) obtained is a type I of IUPAC classification adsorption isotherms (1985), that refers to "microporous solids having relatively small external surfaces (e.g. activated carbons, molecular sieve zeolites and certain porous oxides)". Isotherm presents for pyrolysis temperatures above 325 °C, there is an increasing

quantity adsorbed. While for the treatments 200_2 and 200_4, the curves were similar to *in natura* treatment.

Same results were observed for pore size distribution in Fig. 10b, where the treatments with higher pyrolysis temperatures shows higher volume of higher pores widths. A step change that is noted between 300 – 500 °C in both graphs of porosity, was also reported by Qambrani et al. (2017).

The presence of micro, meso and macropores are important in biochar because these properties may enhance the quality structure of the applied soil. Incorporation of biochar to soil decrease the bulk density, improve the aeration and the water holding capacity (LEHMANN et al., 2011; TOMCZYK; SOKOLOWSKA; BOGUTA, 2020).

Fig. 11 shows the SEM micrographs of the *in natura* and biochar treatments.

Figure 11. Scanning Electron Microscope micrographs for (a) *in natura*; (b) biochar 200 °C, 2h; (c) biochar 200 °C, 4h; (d) biochar 325 °C, 2h; (e) biochar 325 °C, 4h; (f) biochar 450 °C, 2h; (g) biochar 450 °C, 4h.
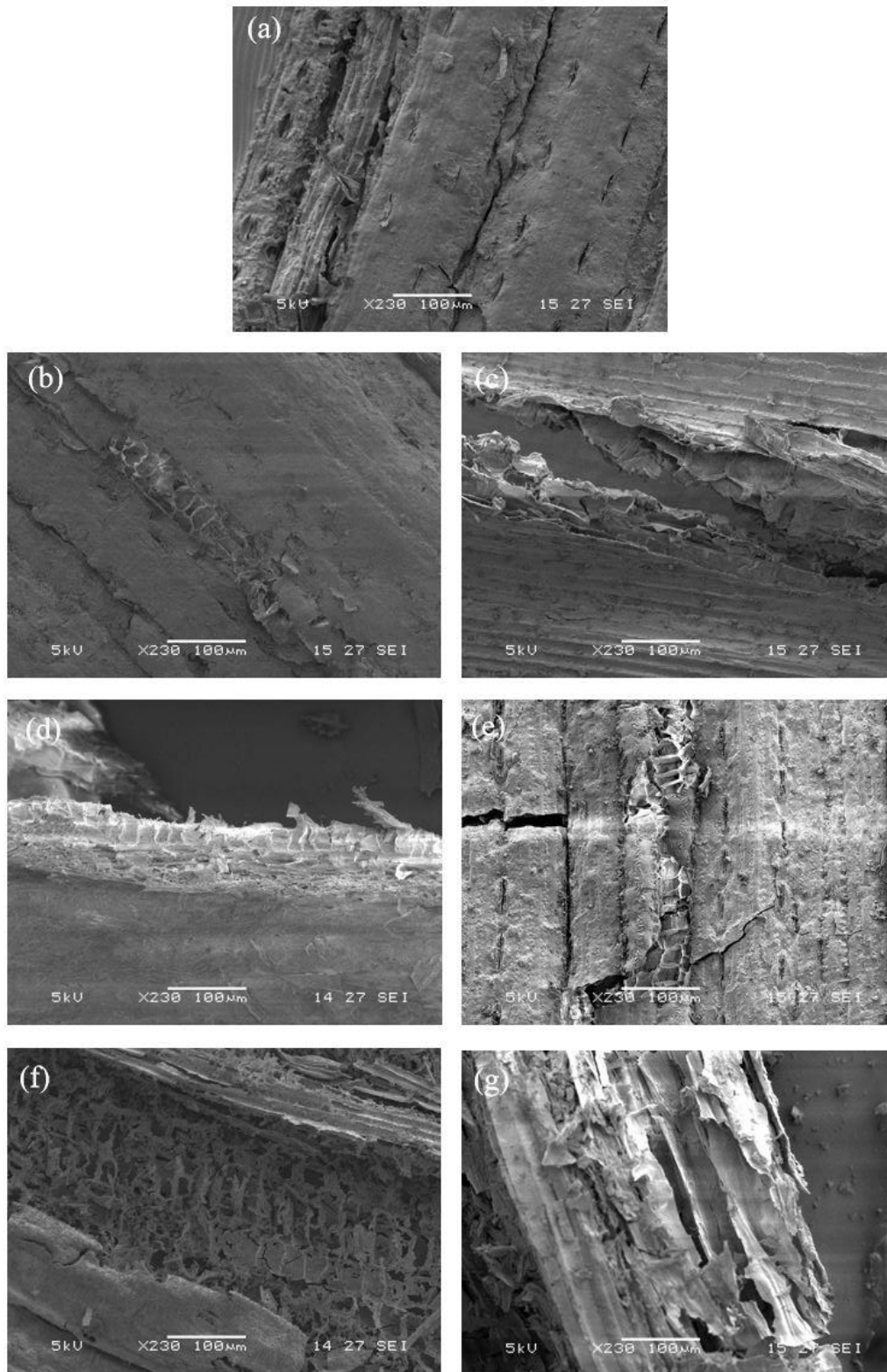


SEM micrographs explore the surface of the material in a morphological characterization (MANYA, 2012). Almost all the surfaces presented in Fig. 11 were found

preserved, except for (f) 450_2 and (g) 450_4. Fig 11 (f) and (g) presented more degraded walls, creating voids cavities.

### 2.3.7. Hydrophobicity

Hydrophobicity of the studied treatments was determined recording the Water Drop Penetration Time (WDPT) and contact angle was applied to evaluate the hydrophobicity of the surface of biochar (Fig. 12).

Figure 12. Water drop penetration time (WDPT) test for sugarcane trash biochar in different pyrolysis temperatures and residence times. t = time that the first image was taken. WDP = time that the sample penetrate or reached the maximum time of the experiment.
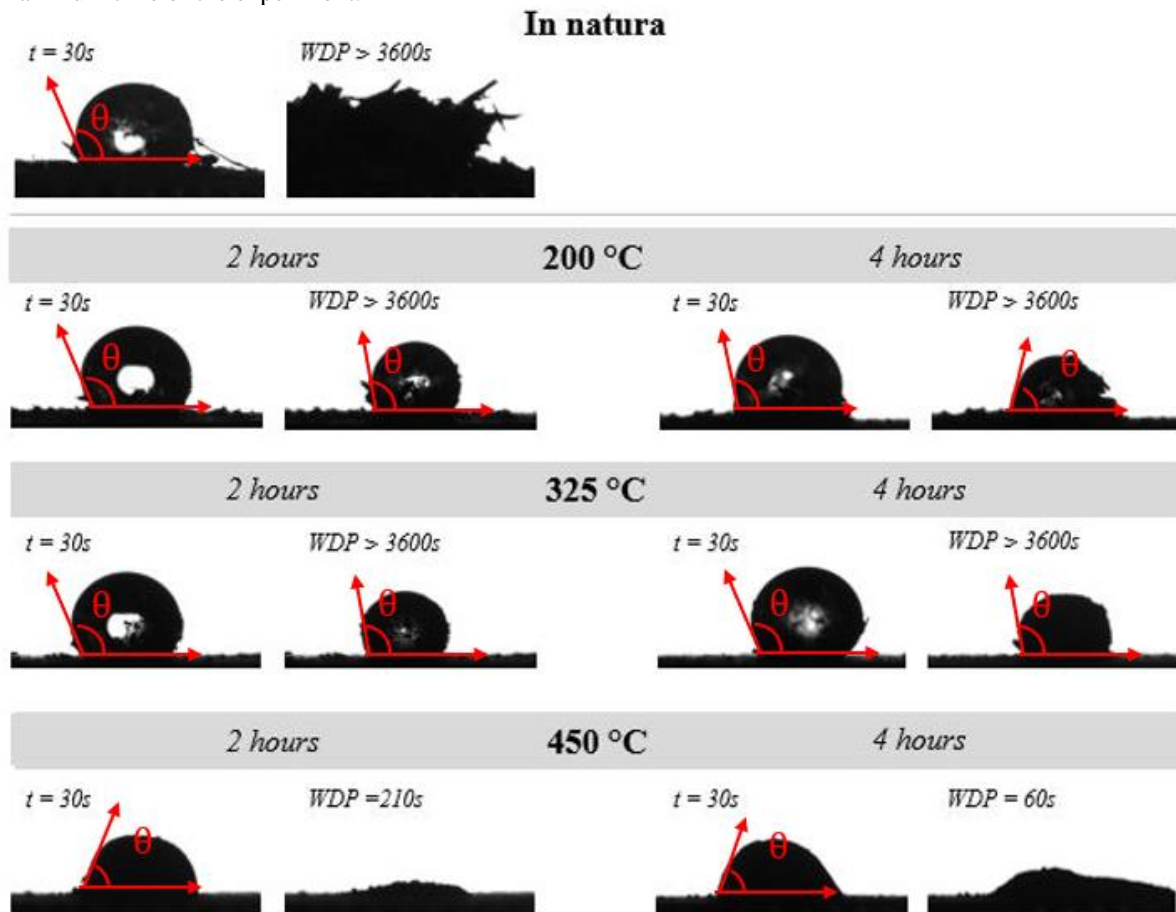


In Fig. 12, $\theta < 90°$ indicated the biochar surface was hydrophilic, and $\theta > 90°$ suggested that the surface was hydrophobic. The initial (t=30s) water contact angle of the *in natura* was $\theta > 90°$ but in the final (t=3600s) $\theta = 0°$, indicating the hydrophilic characteristic. For biochar at 200 °C and 325 °C, the loss of hemicellulose and part of cellulose also reflect on the decrease of hydrophilic groups, turning them hydrophobic (contact angle $> 90°$) (ACHARYA; DUTTA; MINARET, 2015; LI et al., 2018). In case of Li et al. (2018) the raise in torrefaction

temperatures caused higher degrees of hydrophobicity as a result of contact angle larger than 90°.

The images of Fig. 12 of the water drop were taken after 30s of the start time and at the end. According to Bisdom, Dekker and Schout (1993) classification, all the treatments are defined in extremely hydrophobic (>3600s), except for 450 °C treatments.

It was believed that high pyrolysis temperatures increase the hydrophobic character, caused by loss of polar functional groups (hemicellulose and cellulose) and the increase of aromaticity of the material (WEBER; QUICKER, 2018). Despite of this affirmation, the 450 °C treatment decreased their level of hydrophobicity, according to Bisdom, Dekker and Schout (1993) and Sato et al. (2019). Thus, the biochar 450_2 and 450_4 can be classified as strongly hydrophobic and slightly hydrophobic, respectively.

Mao, Zhang, Chen (2019) produced biochar from different feedstock (pine wood sawdust, orange peel, pine needle, rice bran, pig manure) in temperature at 300, 500 and 700 °C. The results showed that biochar hydrophobicity changes according to material and temperature. In general, the water repellency of biochar produced at high temperature was lower than that produced at low temperature. Results exposed by Zornoza et al. (2016) report that crop residue and municipal solid waste biochar became hydrophilic in treatments > 500 °C of pyrolysis temperature. Close to the behavior presented by Zornoza et al. (2016), Sato et al. (2019) studied the WDPT in biochar from açai seeds and obtained the transition for affinity to water at 500 °C of pyrolysis temperature. In this case, the biochar produced at 500 °C in a residence time of 1 hour showed an extremely water repellent character, while for 2h residence time this character was slightly hydrophobic, turning to hydrophilic with 3h residence time.

This behavior of high hydrophobicity at low temperatures is possibly justified by the less pores, low surface area and presence of the aliphatic components agreeing to previous results of porosity and FTIR. According as the temperature increases, there is a gradual degradation of these aliphatic compounds, increase in pore volume and surface area of biochar allowing high capillary force implying greater affinity with water (DAS; SARMAH, 2015; GRAY et al., 2014; SATO et al., 2019; ZORNOZA et al., 2016).

Residence time influenced the reduction of angle contact for pyrolysis temperature of 200 °C and 325 °C. Longer residence time (4h) resulted in shorter contact angle, decreasing the hydrophobicity of the biochar. In pyrolysis temperature 450 °C, occurred a decreasing the hydrophobicity or increasing the hydrophilicity level.

2.4.  CONCLUSION

It can be concluded that the pyrolysis temperature close to the range 325 °C may be enough for soil application, but further analysis in biochar in agriculture should be done. Also, the factor time residence, for this study, just showed difference for hydrophobicity tests. Therefore, considering energy cost, the 2h residence time is more viable for lab-scale biochar production.

In general, the results from proximate analysis, pH, TGA, FTIR, XRD, porosity and hydrophobicity were coherent and complementary. Results obtained clearly define two groups of products, one is *in natura* and 200 °C treatments (200_2, 200_4) and the second is 325 °C (325_2,325_4) and 450 °C (450_2,450_4) treatments. These groups occurred because there is a drastically change in a range of 300-500 °C, when occurs the cellulose degradation, promoting different behaviors for crystallinity, porosity and thermal degradation.

Most of literature recommend the use of high temperatures, above 500 °C, to produce a good quality biochar. This is justified because at high temperatures it is possible to eliminate a significant part of the volatiles, thus increasing the porosity, surface area and aromaticity. However, in a small-scale production, high temperatures may imply in decrease in gravimetric yield and increase costs. In addition, the use temperatures > 700 °C can increase the PAH (poly-aromatic hydrocarbons), that some of them present risks for humans and for environment.

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**CHAPTER 3 – SUGARCANE TRASH BIOCHAR POTENTIAL FOR GREENHOUSE GAS MITIGATION**

**Abstract:** The concern with global warming and climate change has required mitigating actions to reduce greenhouse gases (GHG) emissions. Biochar application for agriculture and forestry can be one strategy to reach this reduction. Therefore, the aim of this study was to assess the potential of sugarcane trash biochar to mitigate GHG emissions through its stability. The sugarcane trash biochar was produced at three pyrolysis temperatures (200 °C, 325 °C and 450 °C) for 2 hours residence time. These samples were characterized by proximate analysis (volatile matter, ash content and fixed carbon content), ultimate analysis (Carbon – C, Nitrogen – N, Hydrogen - H and Oxygen – O content), and pH. The quantification of the released gases ($CH_4$, $CO_2$ and $N_2O$) was done for 5 treatments (CT – soil only, ST – sugarcane trash *in natura*, BC200 – Biochar 200 °C + soil, BC325 – Biochar 325 °C + soil and BC450 – Biochar 450 °C + soil). The results of the characterization of the biochar showed decreased values for H and O and increased values for C and N when pyrolysis temperatures increase. BC325 and BC450 presented the lowest ratios of H/C and O/C, and the lowest Global Warming Potential (GWP).

3.1. INTRODUCTION

Biomass is an organic matter and has its biological cycle, that works in a temperature range around room temperature. Thermal conversion of biomass generates the biochar and make it more stable against microorganisms or mineralization (CHA et al., 2016; MC LAUGHLIN, 2009). The presence of chemical structures like the graphite influence the recalcitrance potential of biochar (REZENDE et al., 2011). Due to the recalcitrance properties, its decomposition occurs slowly, meaning that the carbon input to soil is higher than the carbon output through microbial respiration (VERHEIJEN et al., 2010).

During a complete combustion, more than 90% of biomass is completely converted to $CO_2$, while in biochar around 45-48% is oxidized into $CO_2$. Then, the use of biochar in soils can reduce the emissions of greenhouse gases (CHA et al., 2016; MCLAUGHLIN, 2009; ZAVALLONI et al., 2011). Even, for biochar production when gases are released during pyrolysis, it is possible to capture and provide an energy use for the gas and liquid phase.

In a short-term incubation study, six different produced biochars were amended in two types of soil for 45 days. Biochar treatments produced at the highest temperatures resulted in lowest increase in $CO_2$ emissions (BRASSARD et al., 2018). Other study using biochar for

GHG emission flux noted that the presence of biochar reduced the rate of $CH_4$ oxidation and decreased $N_2O$ production activity (SPOKAS; REICOSKY, 2009).

Knowledge about biochar is becoming more explored, so it is necessary to study how biochar responses to the promised effect are very important. It is known that some characteristics of biomass and pyrolysis are determinant for positive effects or reduction in both soil improvement and climate change mitigation (BRASSARD et al., 2018). Thus, the objectives of this work were to analyze the stability of sugarcane trash biochar in a microcosm at three different pyrolysis temperatures (200 °C, 325 °C, 450 °C) and to check if the biochar is an alternative to mitigate the greenhouse gas emissions.

## 3.2. MATERIAL AND METHODS

### 3.2.1. Soil

Soil was collected in Sorocaba city, São Paulo State, Brazil. Samples were collected with an auger from the topsoil layer (0-20 cm). Soil samples were dried at room temperature, grounded and sieved < 2 mm. Soil texture and density were measured according to Technical Report n.106 (IAC, 2009).

### 3.2.2. Biochar

Biochars were produced from sugarcane (*Saccharum officinarum* L.) trash (green and dry leaves and tops) at different pyrolysis temperatures (200 °C, 325 °C and 450 °C) and residence time of 2h. The sugarcane trash was dried and crushed to 50 mm before pyrolysis. It was used around 18 g of biomass per crucible (with lid). Biochar production had a heating rate of 20 °C min$^{-1}$, under a limited $O_2$ concentration (covered crucibles) in a muffle furnace Jung model 0212 model.

The biochar characterization was done by the proximate analysis, pH, gravimetric yield and ultimate analysis. Proximate analysis, pH and gravimetric yield were described on Chapter 2. The ultimate analysis (C, H, N) was determined using elemental analyzer Perkin Elmer (2400 Series II CHNS/O) in duplicate. The oxygen (O) was calculated by difference (O%= 100- C%, H%, N%, ash%).

### 3.2.3. Incubation

Biodegradability test was realized according to Pitombo et al. (2018) in Bioclima Laboratory in Federal University of São Carlos, Sorocaba Campus. It was used a reagent-type flask of 1000 mL, where the soil and biochar were incubated (Fig. 13). The experiment had 5 treatments, only soil (CT), sugarcane trash *in natura* (ST), biochar 200 °C (BC200), biochar 325 °C (BC325) and biochar 450 °C (BC450) with 4 replicates per treatment. Sugarcane trash *in natura* and biochar application rate was equivalent to 10 Mg ha$^{-1}$ (6.3 g/flask), simulating the residue of the sugarcane harvest in field.

Soil was pre-incubated for 7 days in order to stabilize the gas flux, using the water holding capacity (WHC) of 40% with deionized water. Microcosms were set up with 330 g/flask of collected soil (air-dried). For BC treatment, the biochar was incorporated in the surface layer of the soil (0-5 cm) and for ST, the material was just deposited on the surface of the soil (Fig. 13). After pre-incubation, WHC was increased to 63%. Incubation experiment was carried out for 85 days, with an average temperature of 25 °C.

Figure 13. Microcosms with the samples of soil (CT), soil + in natura sugarcane trash (ST), soil + biochar 200 °C(BC200), soil + biochar 325 °C (BC325), soil + biochar 450 °C (BC450).



### 3.2.4. Gas sampling

The flasks remained open all the time. The flasks were closed just during gas sampling (Fig. 14). It was used a 4-way stopcocked valve for gas sampling. The samples were collected on 1, 30, 60 and 90 min with a 20 mL syringe. The gas flux analysis was done using a gas chromatograph Shimadzu GC-2014 (Shimadzu Co., Kyoto, Japan) equipped with flame induced detector (FID) for carbon dioxide and methane detection and with electron capture detector (ECD) for nitrous oxide quantification.

Figure 14. Schematic method for gas sampling.
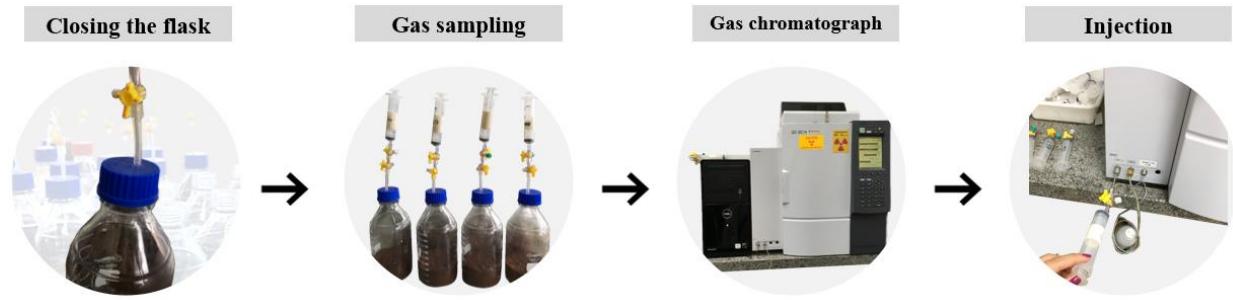


According to Pitombo et al. (2018), GHG fluxes were calculated based on Eq. 2:

$$Flux = \frac{\frac{\Delta gas}{\Delta t} \times n^{\circ}mols}{mass\ of\ material} \times Mgas \times \frac{M \times n}{Mgas} \tag{2}$$

Where:

$\frac{\Delta gas}{\Delta t}$ is the slope of the linear regression of gas concentration vs. time;
$n^{\circ}mols$ is the number of moles of the gas inside microcosm;
$mass\ of\ material$ is the microcosm matrix (soil);
$Mgas$ is the molar mass of the quantified gas;
$M$ is the elemental molar mass;
$n$ is the number of atoms of the element in the gas.

### 3.2.5. Global Warming Potential (GWP)

Global Warming Potential (GWP) emission is a representative form for GHG equivalent for $CO_2$ ($CO_2$-eq). GWP can be obtained by multiplying the emission of GHG by its GWP. The 100 year-GWP (GWP$_{100}$) index was adopted by the United Nations Framework Convention on Climate Change (UNFCCC) and is used as default metric (IPCC, 2014). GWP thus was calculated as Eq. 3:

$$GWP = 1 \times CE\ (CO_2) + 28 \times CE\ (CH_4) + 265 \times CE\ (N_2O) \tag{3}$$

Where:

GWP in µg $CO_2$-eq kg soil$^{-1}$
$CE$ is the cumulative emissions (85-day experiment) for each gas flux $(CO_2)$, $(CH_4)$ and $(N_2O)$ in µg kg soil$^{-1}$;
GWP$_{100}$ for $CO_2$ is 1, for $CH_4$ is 28 and for $N_2O$ is 265.

### 3.2.6. Statistical analysis

The results obtained by cumulative GHG fluxes ($CO_2$, $N_2O$ and GWP) were submitted to analysis of variance (ANOVA) and Tukey Test, using the Software R. For the cumulative $CH_4$ flux was performed a non-parametric test, Kruskal Wallis, due to the p-value $> 0.05$.

## 3.3. RESULTS AND DISCUSSION

### 3.3.1. Soil

Soil characterization is presented in Table 5.

Table 5. Soil characterization for incubation.

| Analysis | Results |
| --- | --- |
| Moisture content (%) | 5.36 |
| Bulk density (g cm$^{-3}$) | 1.11 |
| Water holding capacity | 47.0 |
| Particle density (g cm$^{-3}$) | 2.48 |

The soil was classified with clay texture (32% sand, 16% silt and 52% clay).

### 3.3.2. Biochar characterization

Table 6 presents the results of biochar yield, pH, proximate analysis, ultimate analysis and the H/C, O/C ratios from sugarcane trash in natura (ST) and its biochar produced at 200 °C (BC200), 325 °C (BC325) and 450 °C (BC450) with 2h residence time.

Table 6. Physicochemical characterization for sugarcane trash in natura (ST) and biochars at 200 °C (BC200). 325 °C (BC325) and 450 °C pyrolysis temperatures.

| Analysis | Units | ST | BC200 | BC325 | BC450 |
|---|---|---|---|---|---|
| Biochar yield | % | - | 92.5 (1.2) | 30.6 (0.8) | 27.8 (0.0) |
| pH | | - | 5.57 (0.2) | 7.18 (0.1) | 8.72 (0.0) |
| **Proximate Analysis** | | | | | |
| Volatile matter | % | 76.3 (0.3) | 76.0 (0.8) | 31.1 (0.1) | 18.9 (0.8) |
| Ash content | % | 7.1 (0.4) | 5.3 (0.2) | 17.4 (0.7) | 20.8 (0.3) |
| Fixed carbon * | % | 16.5 (0.1) | 18.6 (0.8) | 51.4 (0.7) | 60.1 (1.0) |
| **Ultimate analysis** | | | | | |
| C | % | 41.4 (1.0) | 43.2 (0.3) | 60.7 (0.1) | 58.1 (0.7) |
| H | % | 6.2 (0.2) | 5.9 (0.1) | 4.1 (0.0) | 3.3 (0.0) |
| N | % | 1.2 (0.2) | 1.1 (0.2) | 2.9 (0.3) | 3.1 (0.3) |
| O * | % | 43.8 | 44.3 | 15.1 | 14.8 |
| H/C | | 1.78 | 1.64 | 0.82 | 0.69 |
| O/C | | 0.79 | 0.77 | 0.19 | 0.19 |

*by difference
Numbers inside parentheses are the standard deviation.

The increase of the pyrolysis temperature revealed the raise of pH from 5.57 to 8.72. The result obtained by pH is related to the increase of ash content, from 5.3 (BC200) to 20.8 % (BC450), because the main composition of the ashes are inorganic materials that may increase the alkalinity of the biochar (YUAN; XU; ZHANG, 2011). The ashes are an undesirable characteristic for energy purposes (NAKASHIMA et al., 2017). However, ashes have a great potential for soil application due to their higher alkalinity, specially for acid soils in Brazil.

Other characteristic that showed the same tendency from ashes is the fixed carbon. The increase in percentage for fixed carbon is caused by the loss of volatiles during the pyrolysis. Thus, the presence of volatile matter or high values of it demonstrate an incomplete thermal degradation, resulting a low potential for soil amendment (MANYA, 2012; ÖZÇIMEN; ERSOY-MERIÇBOU, 2010).

Results for ultimate analysis showed a large increase between BC200 and BC 325 for C and N content, and a decrease for O and H content, this trend was also observed by Mimmo et al. (2014). However the large difference happened between 360 and 370 °C pyrolysis temperature. The van Krevelen diagram (Fig. 15) was used to display these changes from feedstock to biochar. The threshold ratios purposed by European Biochar Certification – EBC (2012) guidelines (H/C – 0.7 and O/C – 0.4) are represented by dashed lines. According to Schimmelpfennig and Glaser (2012) the biochars in this delimited area (H/C < 0.7 and O.C < 0.4) may present a great potential for application in soil due to a better stability.

Figure 15. Diagram of van Krevelen with sugarcane trash in natura (ST) and biochars at 200 °C (BC200). 325 °C (BC325) and 450 °C pyrolysis temperatures. Some values from literature were add for comparison. The arrows are based on Baldock and Smernick (2002) study.
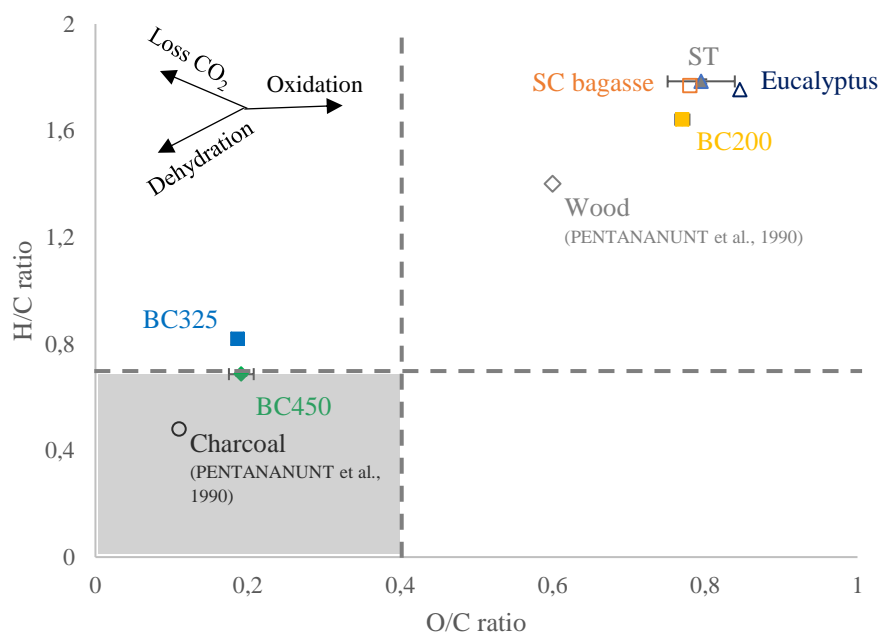


The van Krevelen diagram displays two groups, one is the ST (raw material) and BC200, and the other is the BC325 and BC450. The first group is in a range of 1.6 - 2.0 for H/C and 0.6 - 0.9 for O/C ratio, closer to the other feedstocks such as sugarcane bagasse (SC bagasse), *Eucalyptus* sawdust (Eucalyptus) and not far from wood, presented in a study from Pentananunt, Rahman and Bhattacharya (1990). The ranges obtained correspond to carbohydrates such as cellulose, that is found around ~1.7 for H/C and ~0.8 for O/C ratio (HAMMES et al., 2006; SCHIMMELPFENNIG; GLASER, 2012). BC200 samples may had this behavior because low temperatures are not enough to change organic structures (cellulose), resulting in high values for H/C and O/C ratio (CHUN et al., 2004). These results indicated that BC200 is not recommended for soil application. Despite the appearance of darker color (close to charcoal) BC200 has low stability and will degraded faster.

Group formed by BC325 and BC450 is found in a range of 0.7 to 0.85 for H/C and 0.2 for O/C, these results are closer to the charcoal reported by Pentananunt, Rahman and Bhattacharya (1990). The decrease in H/C and O/C ratios during pyrolysis is related to the loss of hydroxyl, carboxyl, methyl groups and emission of non-condensable gases (volatiles), concentrating the carbon content in the material and increasing its aromaticity degree (AZARGOHAR et al., 2014; SCHIMMELPFENNIG; GLASER, 2012; WINDEATT et al., 2014). The main change for the biochar according to the pyrolysis was the dehydration (BALDOCK; SMERNICK, 2002), observed in Fig. 15 (van Krevelen diagram).

BC450 was within the threshold purposed by EBC (2012), with H/C ratio of 0.69 and O/C ratio of 0.19. According to Spokas (2010) the O/C ratios lower than 0.2 may provide a half-life for biochar larger than 1000 years. The O/C results showed great stability for BC350 (0.19) and BC450 (0.19). Thus, there is a trend that the higher the pyrolysis temperature the lower is the H/C and O/C ratios, the treatments may be classified as BC450 > BC325 > BC200 > ST. Regarding to the stability, the BC450 and BC325 are indicated for soil application.

### 3.3.3. Test of biodegradability

Images of the microcosms top view from all treatments in two different times (15 days and 85 days), are shown in Fig. 16.

Figure 16. Top view from microcosms after 15-days and 85-days.



Through the images of Fig.16 it is possible to observe some signals of decomposition for ST at 85-day. Different for the biochar treatments and control.

The results from the gas chromatograph show the GHG ($CH_4$, $CO_2$ and $N_2O$) released from Soil (CT), sugarcane trash + soil (ST), biochar at 200 °C + soil (BC200), biochar at 325 °C + soil (BC325) and biochar at 450 °C + soil (BC450) as displayed in Fig. 17 ($CH_4$), Fig. 18 ($CO_2$) and Fig. 19 ($N_2O$).

Figure 17. Graph with (a) C-CH$_4$ flux with standard deviation in bars; (b) Cumulative C-CH$_4$ flux for all conditions during incubation.

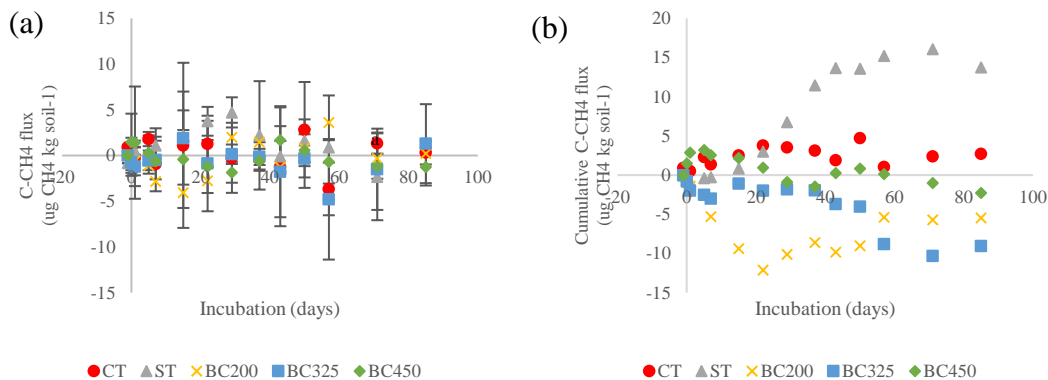

Fig. 17 shows that the CH$_4$ flux until the 60-day varied between -5 and 5 µg kg soil$^{-1}$ and and had its results closer to zero in the last days (60-80 days) of analysis. The cumulative CH$_4$ graph displays the ST as the larger CH$_4$ emitter. On the opposite trend, the BC200, BC 325 and BC450 obtained negative emissions at the end (80 days) of the analysis. Despite of the results of negative emissions (for cumulative data), the addition of biochar to soil did not present any significant result at 5% of significance level, similar to study of Pine sawdust biochar presented by Pokharel et al. (2018).

It is known that methane (CH$_4$) is generated by methanogenic archaea under an anaerobic process (VERHEIJEN et al., 2010). The existence of bacterias that are methanotrophs is important to reduce the amount of CH$_4$ from the soil sinks via microbial oxidation (KNIEF, 2015). Huang et al. (2019) tested the relationship between biochar and methanotroph and methanogenic baterias. And, concluded that the reduction of CH$_4$ emissions may be due to the biochar addition, that also decrease the methanogenic abundance in paddy soils.

The results obtained by cumulative CH$_4$ emissions on Fig. 17 may be justified of the action of methanogenic bacterias in ST, that release CH$_4$ and CO$_2$ for anaerobic digestion. While, the biochar treatments stimulate the CH$_4$ sink capacity with soil aeration and lower bulk density, increasing the methanotrophic bacterias (HUANG et al., 2019).

Figure 18. Graph with (a) C-$CO_2$ flux with standard deviation in bars; (b) Cumulative C-$CO_2$ flux for all conditions during incubation, in days; (c) Cumulative mean values for C-$CO_2$ flux with standard deviation. Different letters indicate significant differences between treatments ($p < 0.05$).
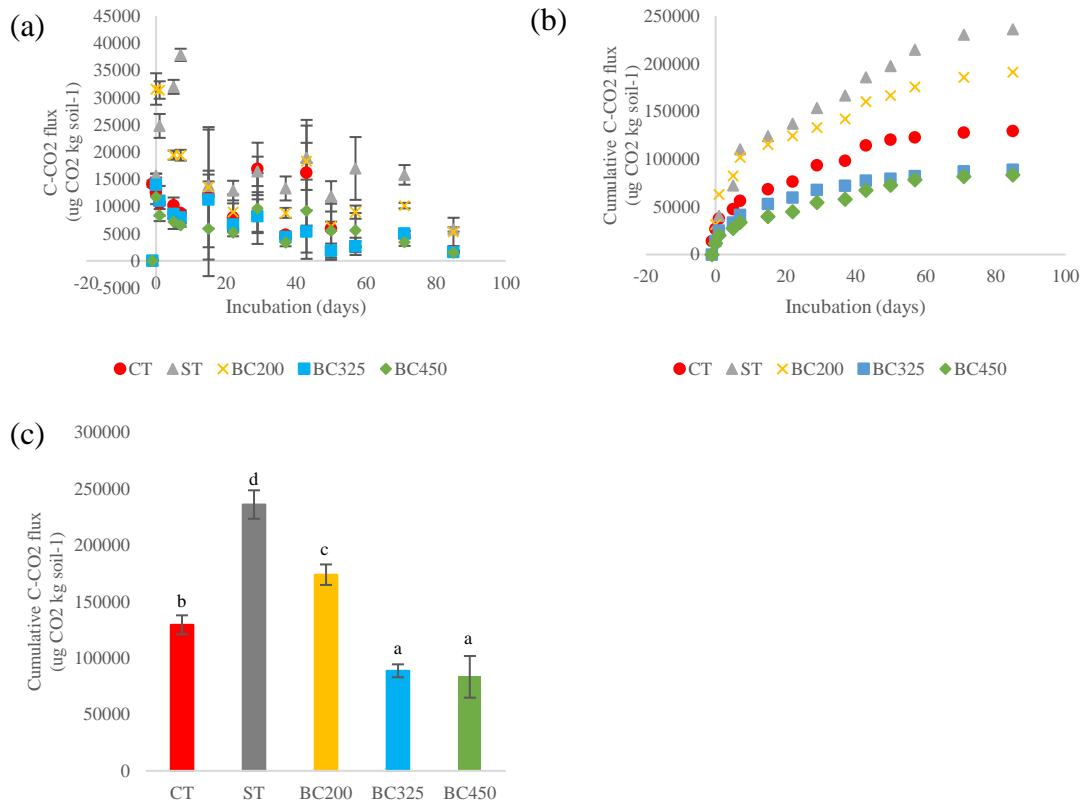


Brassard et al. (2018) considered the $CO_2$ flux as an indicator of short-term stability. Results for $CO_2$ flux are introduced on Fig. 18, which present larger emissions at the first 10 days of gas analysis. Along the time, the $CO_2$ rates were decreasing (BRASSARD et al., 2018). For cumulative $CO_2$ graph, the treatment that released more rates of $CO_2$ was ST>BC200>CT>BC325=BC450. This result was consistent with the H/C and O/C ratios of the samples, showing more stability to BC325 and BC450. The result for ST may have been also contributed by the methanogenic action. The higher rates for ST can be confirmed by Fig. 17, that showed higher degradation process for ST compared to the treatments with biochar. Also, BC200 presented higher $CO_2$ than soil (CT). This result confirm the degradation process of BC200 as discussed in O/C ratio.

According to the data, the increase in pyrolysis temperatures results in lower $CO_2$ emission rates, also observed by Zimmerman (2010). An explanation for this behaviour is that at higher temperatures ($> 300$ °C) the most of volatiles and aliphatic compounds are lost, leading to a more recalcitrant and stable material (SCHIMMELPFENNIG; GLASER, 2012; ZIMMERMAN, 2010). The $CO_2$ emission rates showed that BC325 and BC450 presented lower emission than soil (CT). Even with the lower emission, the results showed that BC325

and BC450 also reduced the soil methanogenic action. Considering the $CO_2$ emission rates, BC325 and BC450 are recommended for soil application.

Figure 19. Graph with (a) N-$N_2O$ flux with standard deviation in bars; (b) Cumulative N-$N_2O$ flux for all conditions during incubation, in days; (c) Cumulative mean values for N-$N_2O$ flux with standard deviation. Different letters indicate significant differences between treatments ($p < 0.05$).
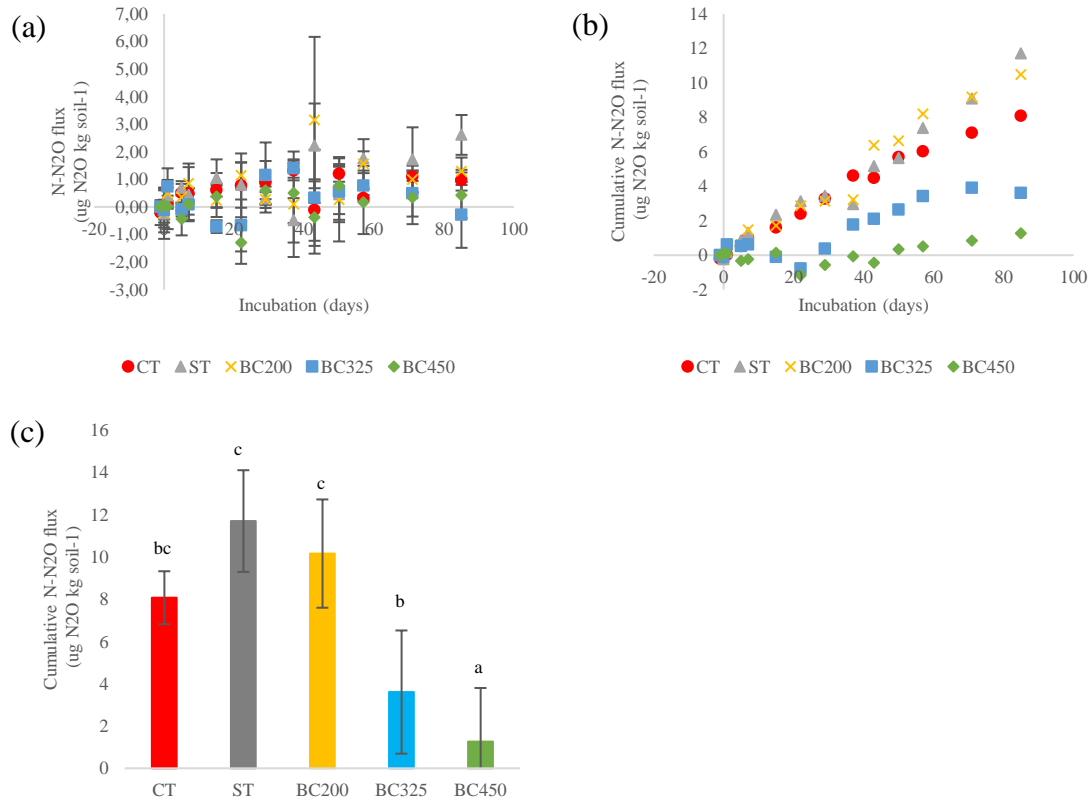


The $N_2O$ production is associated to nitrogen cycle, which the main pathways for releasing $N_2O$ are the processes of nitrification and denitrification (BRASSARD et al., 2018; HUANG et al., 2019). The flux of $N_2O$ is shown in Fig. 19, which almost of all treatments were found in the range around -1 and 2 µg kg soil[-1]. The higher cumulative value for $N_2O$ emission was for ST (11.7 µg kg soil[-1]) and BC200 (10.1 µg kg soil[-1]). Despite no statistical difference from soil, the values indicate a degradation process of ST and BC200. On the other hand, cumulative $N_2O$ emission was reduced by adding the BC325 and BC450. However due to the high deviation there was no statistical difference from the control (CT) and BC325 at a significance level of 5%.

Other studies reported that the biochar application implied in reducing the $N_2O$ emissions from denitrification process (CAYUELA et al., 2013) and in higher rates of N uptake, increasing the N availability (SUN et al., 2017).

Figure 20. (a) Global Warming Potential (GWP) dynamics along the 85-days; (b) Cumulative mean values for GWP flux with standard deviation. Different letters indicate significant differences between treatments (p < 0.05).
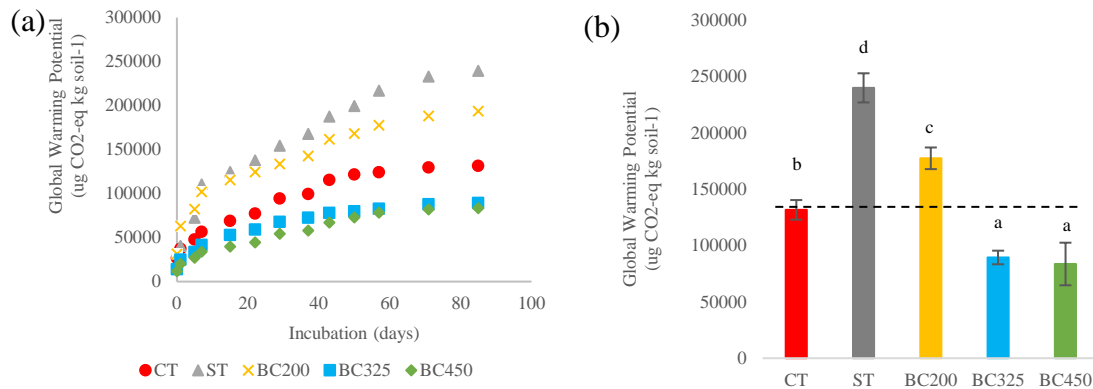


Fig. 20 displays the results of GWP, that is a combination of $CH_4$, $CO_2$ and $N_2O$ emissions. Due to the low rates of the $CH_4$ and $N_2O$, the results of GWP are similar to the $CO_2$ flux (POKHAREL et al., 2018). The results showed that ST and BC200 presented higher emission than soil (control) indicating contribution to GWP. BC325 and BC450 were considered the best treatments and did not differ at 5% of significance. The reduction was 32.1% and 36.5%, respectively, in relation to the control. Then, the sugarcane trash biochar at temperatures of 325 °C and 450 °C can be used as a GHG mitigator, reducing the global warming potential.

## 3.4. CONCLUSION

The factor temperature affected the results for stability of the biochar in soil. The temperature of 200 °C was not enough to make the sugarcane trash more stable and avoid the biodegradation in soil. By contrast, the higher temperatures (325 °C and 450 °C) presented higher stability with a great carbon retention. The biochar produced at 325 °C was the best condition, considering the results of this study and that lowest temperatures consume less energy. Also, the sugarcane trash biochar can be used as a GHG mitigator using pyrolysis temperature equal or higher than 325 °C.

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**CHAPTER 4 – SUGARCANE STRAW BIOCHAR APPLIED TO A SUGARCANE CROP: A POT EXPERIMENT**

**Abstract:** Many studies indicate the use of biochar as a soil amendment, but there are still many doubts about its use and its effects. The objective of this study was to evaluate the use of biochar in different application rates in a pot experiment, using sugarcane plants. The sugarcane straw biochar was produced simulating a small-scale in a furnace, at an approximate temperature of 330 °C for 1h residence time and was applied to a soil with low nutritional load. The sugarcane plants were planted in pots and the biochar application rates were only soil (T0), 1 t ha$^{-1}$ (T1), 5 t ha$^{-1}$ (T5), 15 t ha$^{-1}$ (T15) and 30 t ha$^{-1}$ (T30). Each treatment had 15 plots with 2 plants (30 plants/treatment). The height and diameter of sugarcane plants were measured during the 9 months of experiment, and dry weight was done at the end of the experiment with 5 plants/treatment. The addition of biochar to soil increase the pH of the soil, however the sugarcane plants did not present significant results for increase in diameter, height and dry mass with the biochar application. It was concluded that the biochar addition at this condition influenced the increase in pH and did not caused negative effects for the sugarcane plants.

4.1. INTRODUCTION

The precursor of biochar and its use on soils has an ancient history. It was discovered by the Central Amazonian natives and it was called as 'terra preta' or black carbon. These communities used to use fire when they settle in a territory, and some pyrolyzed materials remained until the natural regeneration of the forest for many years (SOHÍ et al., 2010). In a tentative to reproduce the black carbon properties in the soil, the use of pyrolysis to convert the biomass into biochar was studied.

Biochar has a great ability to retain water and nutrients in the soil, so this material can improve efficiency in irrigation and planting fertilization (FRIEDMAN; TREADWELL; WILKIE, 2012). Biochar application can increase the cation exchange capacity (CEC), neutralizing the acidic soils. Depending on the feedstock, it can present high concentrations of N, P, Ca, K, providing these nutrients to the soil (YUAN; XU; ZHANG, 2011). The carbon content in soil improve the roots penetration and placement and the soil structure, with chemical bonds between biochar and inorganic macromolecular structures (REZENDE et al., 2011).

General application rate for biochar in soil is around 13.5 t ha$^{-1}$, embedded in the topsoil (MATOVIC, 2011). El-Naggar et al. (2018) reported that a minimum application rate and methodology should be defined to make the biochar use economically viable and to increase

the efficiency on the field. According to Kavitha et al. (2018), biochar enables many benefits for agriculture, however these benefits occur in limited conditions, implying further researches. There are several studies about biochar applied to soil. But there is a lack of results of direct effects of biochar on agroforestry production yield.

In Brazil, sugarcane is one of the main crops with a planted area of 8.5 million ha (CONAB, 2019). The proper choice of the planting time is fundamental for the good development of the sugarcane culture, which needs ideal climatic conditions to develop. For its growth, sugarcane requires high water availability, high temperatures and a high level of solar radiation. In Brazil, sugarcane is planted between the months of January and March. In the first three months, the plant begins its development and in winter (cold and dry season) growth becomes very slow for five months (April to August). The greatest development of the plants occurs in the seven subsequent months (September to April). The cycle is completed with maturation at 16 to 18 months (ROSSETTO; SANTIAGO, n.d.).Considering that the main factors for effective productivity of sugarcane are the soil and climate, both need to be managed for the sugarcane cultivation (ROSSETTO; DIAS, 2005; VITTI; MAZZA, 2002). Because of the high biomass production and the removal of the major part of the biomass cover during harvesting, there is a high demand for nutrients (ALVAREZ et al., 1991). Application of mineral nutrients as nitrogen, phosphorus and potassium (NPK) are essential for the maintenance and development of the crop.

The N application rates must to consider the low efficiency for utilization of mineral N (ROSSETTO; DIAS, 2005). The other sources for nitrogen to the plant are from the biological nitrogen fixation and the mineralization. The amount of phosphorus (P) applied in crops only 10 to 30% is absorbed by plants, the P residual is immobilized in soil for next cycles. Because of the low rates of P availability in Brazilian soils, there is a high response from sugarcane crops by the P application (CANTARELLA; ROSSETTO, 2014). The recommended application of $P_2O_5$ for sugarcane plants are 40 to 180 kg $ha^{-1}$ (RAIJ et al., 1996 apud ROSSETTO; DIAS, 2005). In general, the K absorbed by the plants are in forms of cation exchangeable and soil solution. The presence of this nutrient is important for the plant growth, so the main functions are the enzymatic activation and osmoregulation (FAQUIN, 2005). The range of application rate for sugarcane is 80 to 150 kg $ha^{-1}$, depending on the amount contained in soil (ROSSETTO; DIAS, 2005).

Considering the sugarcane crops and sugarcane straw biochar, the objective was to verify the effect of adding sugarcane straw biochar in 5 application rates on the soil and the results on the sugarcane crop yield.

4.2.MATERIAL AND METHODS

### 4.2.1. Biochar production

For biochar production it was collected 30 kg of sugarcane straw (*Saccharum officinarum*) from a plantation located in Sorocaba, SP, Brazil. The material was air-dried for 10 days. Approximately 3 kg of dried biomass was placed in a 20 L metal container with a lid. The production of biochar was done in an oven (firewood), average temperature 330 °C and residence time 1h. The production was repeated 10 times and the total amount of biochar produced was 10 kg.

### 4.2.2. Soil

The soil used in the pots were a low fertility clay soil. It was used 500 kg of clay soil (commercial) mixed with 100 kg of coarse sand (for better permeability). The chemical characterization of the soils with the different rates of application of biochar was carried out before the planting of the seedlings (Apr/2019) and after the end of the experiment (Dec/2019). The characterization of this soil was based on IAC standard (2001) and was carried out at the Faculty of Agricultural Sciences of the São Paulo State University (UNESP).

### 4.2.3. Sugarcane seedling and pot experiment

Sugarcane pre-sprouted seedlings (100 days), clone IAC-SP-97-4039, were donated by IAC – Ribeirão Preto, SP. Seedlings were planted in a pot of 3.8 L (25x17 cm), using soil and 4 different biochar rates: 1 t ha$^{-1}$ (2.3 g pot$^{-1}$); 5 t ha$^{-1}$ (11.3 g pot$^{-1}$); 15 t ha$^{-1}$ (33.9 g pot$^{-1}$); 30 t ha$^{-1}$ (67.8 g pot$^{-1}$). The five biochar treatments were: T0 (only soil); T1 (1 t ha$^{-1}$); T5 (5 t ha$^{-1}$); T15 (15 t ha$^{-1}$); T30 (30 t ha$^{-1}$). Each treatment has 15 plots with 2 repetitions each one (total of 150 plants). Plots were arranged in a completely randomized design (CRD), shown in Fig 21.

Figure 21. (a) Design of the pots with the distribution of the treatments in plots; which each color represents one application rate/treatment (b) Image of the pot experiment in full sunlight.
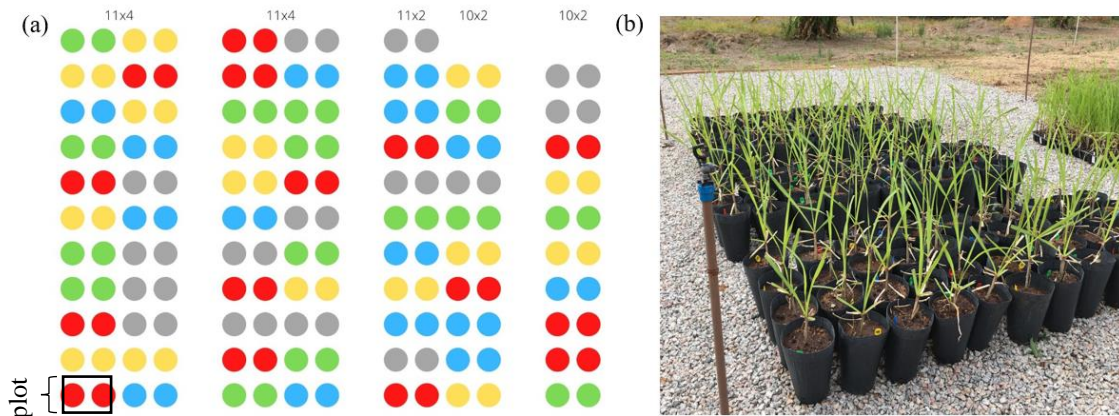


The experiment was carried out from April 2019 to December 2019 and was held in full sunlight (Fig. 21b), at the nursery area of Federal University of São Carlos, Sorocaba, Brazil. The precipitation regime and the average minimum and maximum temperatures for Sorocaba are shown in Fig. 22 (INMET, 2019). It was used a water blade of 14 mm day$^{-1}$ to keep the irrigation in drier periods. There were 2 fertilizer application for all treatments: first in June, of NPK 4-14-8, 500 kg ha$^{-1}$, and second in October, of NPK 20-0-20, 440 kg ha$^{-1}$.

Figure 22. Total precipitation and average minimum and maximum temperature in Sorocaba, SP, Brazil.
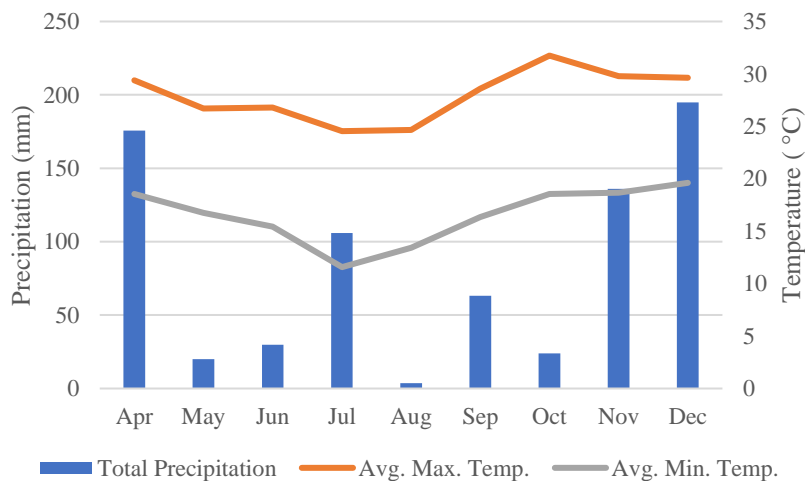


Height and stem diameter measurements of the sugarcane seedlings were monitored every 20 days. After 9 months, 5 plants of each treatment were harvested and washed to remove residual soil, mainly in the roots. The aerial part (plant mass – PM) and the root part (root mass – RM) were placed in an oven at 65 °C. After 72h, the materials were weighted to obtain the dry mass.

### 4.2.4. Statistical Analysis

Height, stem diameter and dry mass of sugarcane was analyzed by Analysis of Variance (ANOVA), due to the p-value < 0.05, the non-parametric test, Kruskal Wallis was performed in R software.

4.3. RESULTS AND DISCUSSION

### 4.3.1. Soil chemical characterization

Table 7 presents the results obtained by the soil chemical characterization with the different biochar application rates of T1 (0 t ha⁻1), T1 (1 t ha⁻¹), T5 (5 t ha⁻¹), T15 (15 t ha⁻¹) and T30 (30 t ha⁻¹).

Table 7. Characterization of the soil used before and after the pot experiment.

| | Treat. | pH CaCl$_2$ | SOM g dm$^{-3}$ | P$_{resin}$ mg dm$^{-3}$ | H+Al | K | Ca | Mg | BS | CEC | V% | B | Cu | Fe | Mn | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | – — – – – – – mmol$_c$ dm$^{-3}$ – – – – – – | | | | | | | – – – – – – – – mg dm$^{-3}$ – – – – – – | | | | |
| Before | T0 | 4.74 | 25 | 42 | 51 | 0.7 | 56 | 3 | 60 | 111 | 54 | 0.9 | 1.6 | 21 | 25.6 | 19.0 |
| | T1 | 4.77 | 27 | 42 | 57 | 1.2 | 51 | 4 | 56 | 114 | 50 | 1.01 | 1.8 | 21 | 27.3 | 25.4 |
| | T5 | 4.88 | 25 | 70 | 50 | 3.4 | 85 | 5 | 93 | 143 | 65 | 1.20 | 1.7 | 21 | 22.7 | 26.3 |
| | T15 | 5.05 | 25 | 48 | 43 | 5.9 | 44 | 5 | 55 | 98 | 56 | 0.95 | 1.5 | 19 | 17.2 | 20.5 |
| | T30 | 5.78 | 26 | 52 | 30 | 12.3 | 40 | 8 | 60 | 89 | 67 | 0.98 | 1.8 | 19 | 16.3 | 22.1 |
| After | T0 | 5.72 | 29 | 52 | 31 | 2.4 | 53 | 13 | 68 | 100 | 68 | 0.21 | 2.1 | 20 | 6.0 | 15.6 |
| | T1 | 5.50 | 28 | 43 | 30 | 2.5 | 68 | 10 | 81 | 110 | 73 | 0.24 | 2.3 | 19 | 6.2 | 18.4 |
| | T5 | 6.14 | 28 | 44 | 26 | 2.3 | 53 | 12 | 67 | 93 | 72 | 0.24 | 2.7 | 21 | 7.6 | 17.6 |
| | T15 | 5.55 | 32 | 57 | 35 | 1.8 | 50 | 11 | 63 | 98 | 64 | 0.22 | 4.0 | 24 | 9.0 | 22.7 |
| | T30 | 6.01 | 30 | 31 | 25 | 2.3 | 53 | 15 | 70 | 95 | 73 | 0.22 | 2.0 | 20 | 7.5 | 14.1 |

SOM (Soil Organic Matter), BS (Sum of Base), CEC (Cation Exchange Capacity – meq.100cm$^{-3}$), V% (Base Saturation)

In Table 7, the characterization of pre-planting presented an increase in pH values according to the increasing of biochar application rate in the soil. The pH for treatment T0 was 4.7 and T30 was 5.8, representing an increase of 1.1 units. The liming effect on the soil remained until the end of the experiment (9 months). According to Lee et al (2013), the use of biochar to neutralize acid soils can improve the soil quality and increase the productivity of crops. Other studies also present an improvement of pH with biochar addition, Chan et al. (2007) had 1.22 units of increased pH for biochar without N fertilizer and 0.61 units for N fertilizer application.

According to Chinelato (2019) pH < 4.5 (high acidity) and 4.6 - 5.5 (medium acidity) and for sugarcane is recommended pH 5.5 - 7.0. This trend is important because, the pH interferes in the availability of nutrient on soil (SFREDO; BOKERT, 2004).

The results for SOM were 25 - 32 g dm$^{-3}$, thus the values are within the recommended by Penatti (2013) SOM > 15 g dm$^{-3}$. According to Cantarella and Rossetto (2014) the nitrogen available in soils are provided by the mineralization of soil organic matter (SOM), but this process depends on levels of temperature and humidity in soil.

Base saturation (V%) is the proportion of the cation exchange capacity (CEC) occupied by the bases (Ca, Mg, K, Na). Soils with base saturation greater than 70% indicate that there is no need for liming (SOBRAL et al, 2015). The base saturation results (V% = 54) showed that liming is necessary for the soil. The addition of biochar in soil increased the V% indicating that biochar has a liming effect in soil.

There was also noted an increase of potassium (K) with the increasing of biochar application rate for the period pre-planting. At the end of the experiment the K content presented an average of 2.4 mmol$_c$ dm$^{-3}$ for T0, T1, T5, T30 and T15 was 1.8 mmol$_c$ dm$^{-3}$. The after-planting analysis of K was influenced by the two NPK fertilizations.

The high concentrations of P did not present any tendency related to the biochar application. The recommended value for sugarcane crops is P = 30 mg dm$^{-3}$ (PENATTI, 2013).

The manganese (Mn) showed lower values as biochar increased: 27.3, 22.7, 17.2 and 16.3 mg dm$^{-3}$ for T1, T5, T10 and T30 respectively. The same behavior was observed for aluminum (Al): from 57 mmol$_c$ dm$^{-3}$ (T1) to 30 mmol$_c$ dm$^{-3}$ (T30). The results can be explained by the liming effect of biochar. According to Cantarella and Rossetto (2014) the liming effect may be helping to neutralize the Al and Mn. The amount of Mn can be harmful in acidic soils, which its availability increases and can reach toxic levels. The results showed that Mn values were above the recommended by Penatti (2013) Mn = 5 mg dm$^{-3}$ and values > 6 mg dm$^{-3}$ are considered high level.

Calcium is essential for sugarcane crops and is important for the root system development and increase the availability of some nutrients, such as H$_2$PO$_4^-$ (VITTI; MAZZA, 2002). The pre and post-planting for Ca were above the ideal value. For magnesium, the pre-planting presented a deficiency for all treatments except for T30, and after, the values increased without adding mineral Mg.

Immobile nutrients as copper (Cu) and zinc (Zn) are micronutrients and are also recommended for sugarcane plantation, the presence of Cu should be > 0.8 mg dm$^{-3}$ and for Zn > 1.2 mg dm$^{-3}$ (PENATTI, 2013). But, the increase values for Cu from pre-planting and after

planting may be explained by some contamination in NPK applied. According to Milinovic et al. (2008), concentrations of Pb, Cd, Cu and Mn can be found on some NPK fertilizer. The range observed for Cu values was from 7.1 to 974.7 mg kg-1, and the highest concentrations were noted in coloured NPK.

Almost the elements in Table 7 presented values above the minimum recommended by Penatti (2013) for sugarcane. Liebig's "Minimum Factor" Law mentions that the mineral substance in lower relative concentration determines the limit for growth and yield. In this sense, two elements (K and Mg) in pre-planting did not achieved the minimum values recommended by Penatti (2013), K (lower = 0.8 - 1.5, ideal= 3) and Mg (lower =< 4, ideal=8). The results showed that biochar increased the values for K. The treatments T5, T15 and T30 achieved the ideal amount for K. The results for K (1.8 - 2.5) at the end of the experiment showed values over the minimum (K > 0.8) but lower than ideal (K=3). The complementary NPK application was done three months before. Also, the biochar increased the values for Mg. All treatments with biochar achieved the minimum level for Mg and treatment T30 achieved the ideal (Mg=8).

For pre-planting characterization, the addition of biochar did not affect directly the results for soil characterization, except for the increase of pH, K and Mg. The decrease of Mn may be related to higher levels of pH, because pH regulates the availability of some nutrients (ROSSETTO; DIAS, 2005). The results for post-planting preserved the characteristics of higher pH and liming effect.

### 4.3.2. Plant responses

Fig. 23 showed the (a) biochar applied to the soil; (b) after sugarcane planting, (c) before harvesting, (d) sugarcane samples.

Figure 23. Evolution of the sugarcane: (a) biochar added to soil; (b) planted sugarcane day-1; (c) Developed sugarcane day-258; (d) sugarcane samples from each application rate.



Through the images (Fig. 23b and 23c) it is possible to verify the growing of the plants. Despite the notable growing, all the plants on Fig. 23c were similar for aerial parts and root. It can be explained by the pot size that limited the full development of the plants (aerial parts and root), highlighted by the size of the roots in Fig. 23d. Sugarcane roots are used to explore deeper layers in search for nutrients (ROSSETTO; DIAS, 2005) and the pot was a barrier for a plant (age 11 months).

The results of the measurements of the diameter and height are shown in Fig. 24 and 25, respectively.

Figure 24. Results for yield of the diameter and the first measure (initial).
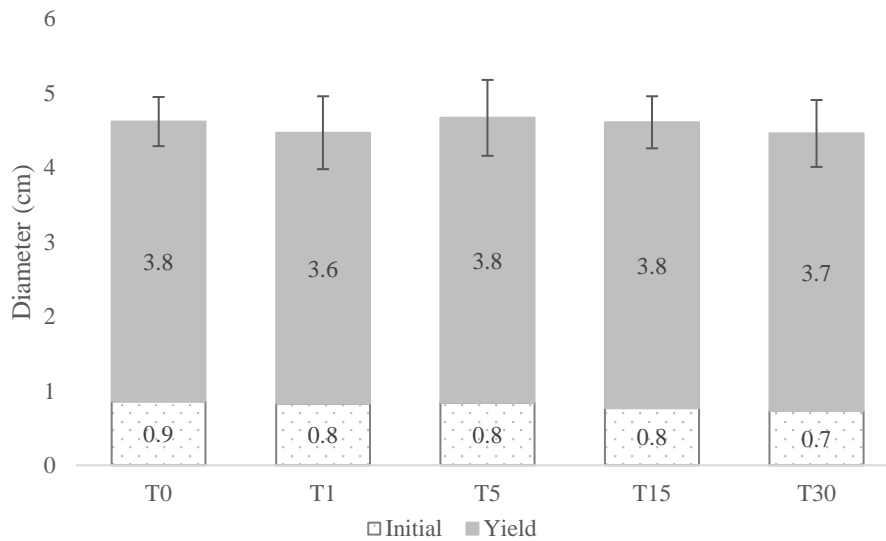


The results for diameter (Fig. 24) in all treatments did not were different at 5% significance level. From de beginning to end of the experiment, T0 even without biochar application presented the same mean for diameter as the others. The addition of biochar did not interfere nor positive or negatively in sugarcane diameter growing.

Figure 25. Results for yield height and first measurement (initial).
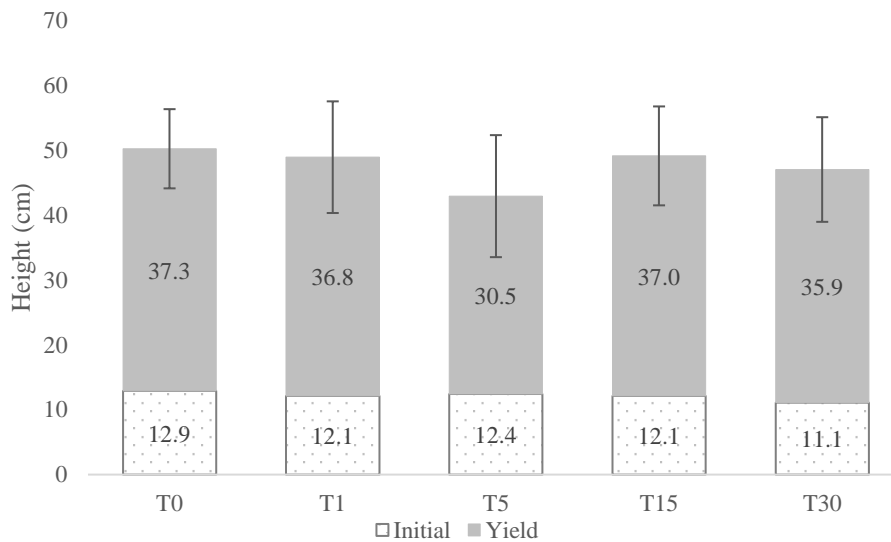


Statistically, the height (Fig. 25) also did not present different among all treatments. The height growth had the same behavior presented for diameter. The T0 without addition of any biochar showed the same mean for height. The biochar application had, statistically, no response for height improvement.

The results for dry mass for plant and roots are shown in Fig. 26.

Figure 26. Dry weight for Plant Mass (PM) and Root Mass (RM).
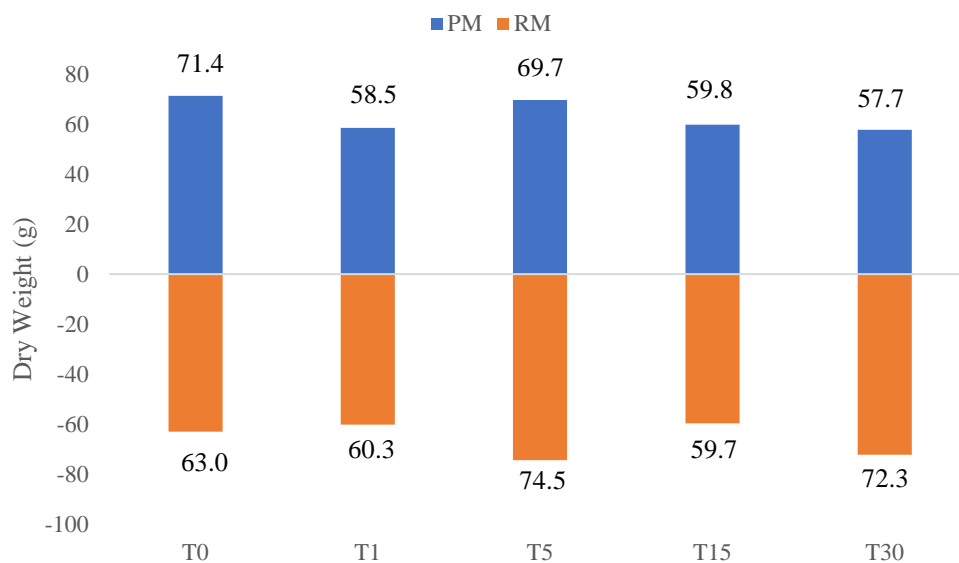


The results of Fig. 26, for plant mass (PM) and root mass (RM), also did not present statistical difference among treatments. The biochar did not interfere in plant dry mass (aerial and root). Chan et al. (2007) detected that even the highest application rate (100 t ha$^{-1}$) of green waste biochar, did not present significant result for radish dry weight yield.

Also, other studies applied biochar in the soil and the results did not showed statistical difference. Horáck, Simanský and Aydin (2020) studied the impacts of biochar application in grain yields of barley, wheat and corn in a three years field experiment. The treatments were biochar at three doses (0, 10 and 20 t ha$^{-1}$) and three levels of N fertilization (0, 1$^{st}$ and 2$^{nd}$ intensity of N). The results showed that soil pH significantly increased with biochar application. According to the authors, the ability of biochar to increase crop yields was observed in the first two years and this effect was almost eliminated in the last year. But, in most cases, differences in grain yields were statistically no significant.

Starr, Deng and Helenius (2020) simulated response of sorghum biomass and grain yield to biochar amendment. The used parameter in the model are site, soil, cropping management data and 4 biochar treatments. The results showed that although grain yields were higher in wetter years, they were unaffected by biochar treatments. The simulation demonstrated the limited response of grain yield to biochar. According to authors, careful selection of sorghum variety and planting date may be a more effective means of improving yields than applying biochar.

Blatt-Janmaat, MacQuarrie and Sit et al (2020) used biochar-microbial composite to enhances barley growth. The topsoil (control) were prepared with 5% (v/v) of biochar and biochar-composite microbial. After nine weeks the shoots were cut right above soil line. The

results showed significant differences in shoot lengths for biochar treatment compared to the control (no biochar). However, an opposite trend was observed for the weight. The results showed no differences in weight for biochar treatments compared to the control (no biochar). According to the authors, the reason why results did not match the other findings include differences in the amount of biochar utilized and the nutrients for plant growth. Also, the increased surface area of the biochar could result in bacterial secretions being trapped in soil (biochar) and not reaching the plant.

In this study, the results showed no statistical difference between treatments for diameter, height and dry mass of sugarcane. According to Rossetto and Santiago (n.d.) the sugarcane growth is very slow during the winter (April to August). The experiment was carried out from April to December. During the first five months (Fig. 22) the plants development was limited by weather (winter conditions). This may have blocked the possible biochar effects.

### 4.3.3. Fertilizer application

The first application of NPK 4-14-8 fertilizer corresponds to a dosage of 20 kg of N, 70 kg of $P_2O_5$ and 40 kg of $K_2O$. Considering the recommendation for sugarcane crops by Rossetto and Dias (2005) and soil chemical characterization results, the level of nitrogen should be more than 30 kg and the potassium from 40 to 150 kg. The second application was used the NPK 20-020, in order to solve this lack of nitrogen and potassium. In Fig. 27 is possible to follow the sugarcane development along the 9 months.

Figure 27. Mean values of height and diameter along time with NPK applications.
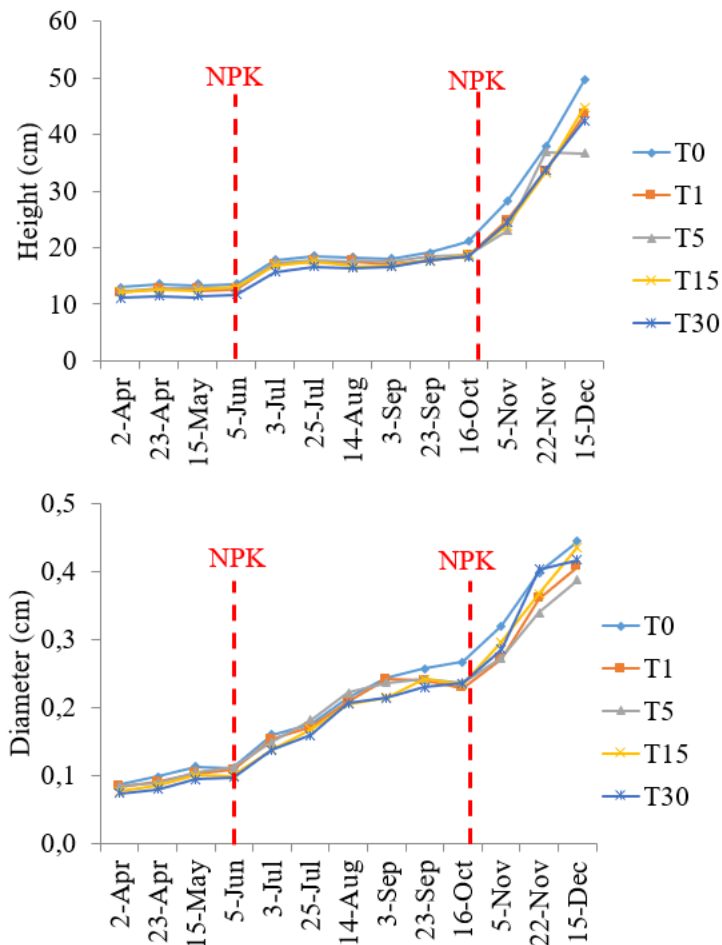


Fig. 27 shows the development of height and diameter of the sugarcane plants. It was possible to observe that the different biochar application rates did not affected for the plant growing. During the first three months the growth (height and diameter) was very slow, close to zero. In June, the plants start to present signs of malnutrition. To prevent the death of the plants, fertilization was carried out. The dosage for NPK 4-14-8 (500 kg ha^{-1}) was lower than the recommended. The purpose was to supply the enough amount to survival. The plants response to NPK application was quickly. But full development was limited by climate (winter). The second application dosage for NPK 20-0-20 (440 kg ha^{-1}) met the recommended by Rossetto and Dias (2005). After the second NPK addition (Oct/spring-summer) and without the climate restriction there was a sharp increase.

Figure 28. Sugarcane leaves with 258 days presented some symptoms of deficiency (indicated).



Despite of the NPK applications, the image of Fig. 28 presents symptoms of nutrients deficiency, indicated by the leaves. By a visual diagnosis, the chlorosis and necrosis with "V" shape on the tip of the leaf are caused by N deficiency. Also, the lack of N turns the leaves in light green and yellow coloration (McCAULEY; JONES; JACOBSEN, 2011; ROSSETTO; SANTIAGO, n.d.). According to McCauley, Jones and Jacobsen (2011), the deficiency of potassium in sugarcane plants cause a chlorosis along the leaf margins leading to a necrosis. The results of soil analysis (Table 7) showed that K values for all treatments are lower than the ideal K value recommended for sugarcane.

There are several studies about biochar applied to soil. Some researchers reported the improvement of soil properties, such as Rafael et al. (2019) that tested baby corn peel biochar, branches of mango tree biochar and rice husk biochar in combination of 3 doses of NPK fertilizer. The authors concluded that the soil chemistry was improved mainly by baby corn peel and mango tree biochar in combination of fertilizer. Chan et al. (2007) applied green waste biochar in a radish pot experiment with and without N fertilizer. They found that results for pH, organic carbon and CEC increased with the addition of biochar.

Other study with maize yield with five fertilizers: ammonium nitrate (AN), urea (U), BN51/10 (51% Biochar + 10% N), BN40/17 (40% Biochar + 17% N), BN29/20 (29% Biochar + 20% N) and control (without N). The maximum rate of biochar was 408 kg ha$^{-1}$. The results showed that highest yields were achieved by BN51/10 and BN40/17. According to the authors a slower N release by the biochar BN51/10 and BN40/17 may explain the greater maize yields.

On the other hand, BN29/20 may not have presented a slow release of N, because the low percentage of biochar (29% biochar + 20% N), that resulted in higher $NH_3$ volatilization. The results indicated that, although the biochar + N contained lower concentration of N than a commercial (urea), they have equal agronomy efficiency with and an environmental performance superior to the conventional sources (urea) (PUGA et al, 2020).

## 4.4. CONCLUSION

The application of the sugarcane straw biochar in different application rates did not generate significant results for the sugarcane plants, however it did not interfere negatively in its development. The application of biochar had the effect of liming on the soil, showing itself as a potential to replace calcium and magnesium, which are widely used to correct Brazilian acid soils. Other studies should be carried out in a field scale, due to the pot used in this experiment acted as a barrier for the development of the plant.

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**CHAPTER 5 – GENERAL CONCLUSIONS**

Research on biochar has become increasingly popular. The search for the keyword 'biochar' based on 'sciencedirect.com' had 167 scientific papers published from the first publication on biochar until 2010. For this decade, the number of publications reached 13,426, with year-2019 having the highest number of publications (3,298). The publications are distributed in the areas: Environmental Sciences (42%), Agronomy and Soil Science (22%), Engineering Chemical (18%), Energy Fuel (16%) and others (2%). Considering the publications per countries: China (39%), USA (17%), Australia (6%), South Korea (5%), Brazil (3%). The list includes 109 countries. Despite the concentration in China and USA, the dispersion indicates that the topic of biochar arouses interest worldwide.

The growing demand for understanding how this material responds to soil, water and air is due to that there are a multitude of raw materials, production conditions, and places to biochar be applied. The results obtained by each chapter in this work were complementary, from its production and characterization, through biodegradation and ending with its behavior in soil application in sugarcane pot experiment. First, the use of sugarcane trash and other biomasses that have high levels of inorganic materials has great potential when applied to the soil. These raw materials create several problems in energy production, which is usually the most common destination for them. Being its application to the soil, the inorganic matter can increase the alkalinity of the soil and provide nutrients.

Pyrolysis, which is the thermal conversion of biomass into biochar, can also simultaneously produce bio-oil and biogas, making use of almost 100% of the material. Thus, the minimum conditions to produce biochar in this work that reached the best values for yield, carbon content and stability were stablished by 325 ° C and 2 hours of residence time.

The application of biochar to the soil did not generate significant results in terms of yields from sugarcane planting, but the presence of biochar did not have negative effects on planting. An increase in soil pH was observed in the pre-planting period and perhaps the biochar can maintain pH levels until after planting (more than 9 months). Further studies on larger scales should be carried out to verify the effects of biochar without the physical limitation of the pot. In general, biochar is a feasible destination that brings positive responses to the soil and presents a high degree of stability, being able to exceed 1000 years of half-life.