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CAMPUS DE SOROCABA
PROGRAMA DE PÓS-GRADUAÇÃO EM
"PLANEJAMENTO E USO DE RECURSOS RENOVÁVEIS"

GABRIELA TAMI NAKASHIMA

USE OF SUGARCANE TRASH FOR SOLID BIOFUEL PRODUCTION: PHYSICOCHEMICAL CHARACTERIZATION AND INFLUENCE OF STORAGE TIME

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Dissertação apresentada ao Programa de Pós-Graduação em “Planejamento e uso de recursos renováveis”, para obtenção do título de mestre em “Planejamento e uso de recursos renováveis”.

Orientação: Prof. Dr. Fábio Minoru Yamaji
Co-orientação: Hiroyuki Yamamoto

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Dissertação apresentada ao Programa de Pós-Graduação para obtenção do título de mestre em Planejamento e Uso de Recursos Renováveis.
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Dedico este trabalho aos meus
queridos pais, Olga e Mario, à minha irmã,
Flávia, e aos meus avós (in memoriam).

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“Que os vossos esforços desafiem as impossibilidades, lembrai-vos de que as grandes coisas do homem foram conquistadas do que parecia impossível. ”

Charlie Chaplin

RESUMO

NAKASHIMA, Gabriela Tami. Uso do palhiço da cana-de-açúcar para a produção de biocombustíveis sólidos: Caracterização físico-química e influência do tempo de estocagem. 2016. 59 f. Dissertação (Mestrado em "Planejamento e uso de recursos renováveis") – Centro de Ciências e Tecnologias para Sustentabilidade, Universidade Federal de São Carlos, Sorocaba, 2016.

No manejo da cana-de-açúcar era comum a utilização do fogo para facilitar o corte e colheita da cana. No entanto, a Lei 11.241/02 do estado de São Paulo prevê a eliminação gradual da queima da palha da cana-de-açúcar. O maior produtor de cana-de-açúcar do Brasil é o estado de São Paulo, que possui aproximadamente 4,7 milhões de hectares de área plantada. É estimado que 1 hectare produza cerca de 14 toneladas de palha. Logo, as usinas vêm tentando incorporar esta palha na queima para geração de energia, juntamente com o bagaço. Porém, as altas concentrações de impurezas minerais estão impossibilitando seu uso para fins energéticos. O trabalho teve como objetivo o estudo da influência do tempo de estocagem e da granulometria na caracterização físico-química do palhiço da cana-de-açúcar. Foi utilizado o palhiço de cana-de-açúcar da superfície e do interior do fardo coletados em diferentes períodos de estocagem, 0, 1 e 2 anos. O material coletado foi separado em 4 granulometrias diferentes (> 0,420mm, 0,250-0,420mm, < 0,250mm e mix). As análises realizadas foram a distribuição granulométrica, a análise imediata, o poder calorífico superior (PCS), a análise química dos componentes das cinzas, as imagens no Microscópio Eletrônico de Varredura (MEV), o teor de lignina Klason, a holocelulose e os extrativos. Houve variações nos resultados do teor de cinzas com as diferentes granulometrias. Observou-se maior concentração de impurezas minerais nas partículas mais finas (< 0,250mm). O PCS variou entre 15,9 a 18,3 $MJ.kg^{-1}$ e não apresentou diferença estatística para os tratamentos. Os resultados indicam que a palha de cana-de-açúcar apresenta problemas relacionados às impurezas minerais, que dificultam e restringem seu uso como combustível sólido na indústria. A granulometria da palha interferiu nas suas características físico-químicas. O palhiço pode ser estocado no campo e o tempo de estocagem não interferiu na qualidade para o uso como combustível sólido.

Palavras-chave: Impurezas minerais, briquetes, granulometria, poder calorífico superior.

ABSTRACT

NAKASHIMA, Gabriela Tami. Use of sugarcane trash for solid biofuel production: Physicochemical characterization and influence of storage time. 2016. 59 f. Dissertação (Mestrado em "Planejamento e uso de recursos renováveis") – Centro de Ciências e Tecnologias para Sustentabilidade, Universidade Federal de São Carlos, Sorocaba, 2016.

In the sugarcane plantation it was common to use fire to facilitate the cutting and harvesting of sugarcane. However, Law 11,241 / 02 in São Paulo State provides the gradual elimination of this straw burning of sugarcane. The largest producer of sugarcane in Brazil is the São Paulo State, which has about 4.7 million hectares of planted area. It is estimated that one hectare produces about 14 tons of trash. Therefore, the mills have been trying to incorporate this trash in burning with the bagasse for power generation. However, high concentrations of mineral impurities are impossible its use for energy purposes. The aim of the study was to investigate the influence of storage time and particle size in the physicochemical characterization of the sugarcane trash. It was used the sugarcane trash inside and outside of the bale collected at different storage time (0, 1 and 2 years). The collected material was separated into four different particle sizes (> 0.420mm, 0.250-0.420mm, < 0.250mm and mix). The analyzes involved particle size distribution, proximate analysis, the high heating value (HHV), the chemical analysis of the components of the ashes, the images in the Scanning Electron Microscope (SEM), the Klason lignin content, the holocellulose content and extractives. There were variations in the results of the ash content with different particle sizes. It was observed a higher concentration of mineral impurities in smaller particles (< 0.250mm). The HHV varied from 15.9 to 18.3 $MJ.kg^{-1}$ and showed no statistical difference for the treatments. The results indicate that the sugarcane trash presents problems related to mineral impurities which constrain its use as a solid fuel in the industry. The particle size interferes in their physicochemical characteristics. The trash can be stored in field and the time storage did not affect the quality for use as solid biofuel.

Keywords: Mineral impurities, briquettes, particle size, high heating value.

SUMÁRIO

CHAPTER 1 – INTRODUCTION

1.1. GENERAL INTRODUCTION

The work is divided into four chapters to the study of sugarcane leaves and tops (straw, also known as trash). Chapter 1 contextualizes the issue of elimination of sugarcane trash in the pre-harvest. Chapter 2 presents the study of the influence of particle size and storage time on ash content in sugarcane trash. Chapter 3 focuses on the chemical profiling of trash and the influence of storage time. And Chapter 4 presents a general conclusion about the use of sugarcane trash for solid biofuel production.

The study was conducted based on the problem observed in a sugarcane farm located in Ibaté city – SP state. The farm total area is 800 hectares (ha). It is estimated an amount of 12.5 ton of trash per ha/year. Around 50% is recovery by the bailer. In a tentative to comply with the law established in São Paulo State, the gradual elimination of the use of fire in the sugarcane pre-harvest, sought alternatives to the large amount (10,000 ton/year) of trash left in the field.

The first alternative to the use of trash would be leave it on the ground to prevent loss of water and to avoid soil erosion. But this trash ends up attracting insects such as spittlebugs. In this case, the application of pesticide is required, resulting in high cost for this operation.

Another alternative would be the recovery of this trash in bales for energy purposes. However, this practice also involves costs: the purchase of balers and other machines. One way to add value to the trash would be the briquetting process. In briquetting, the raw material is densified and has improved uniformity issues in the final product, storage, handling and transport.

The drawback found in this situation, is the presence of contaminants in the material, which can wear the briquetting machine and other equipment used in sugarcane process. Then, sugarcane trash is a material that has a technical problem in the production of briquettes. Therefore, it sought to explore where these contaminants were more present in this raw material.

1.2. LITERATURE REVIEW

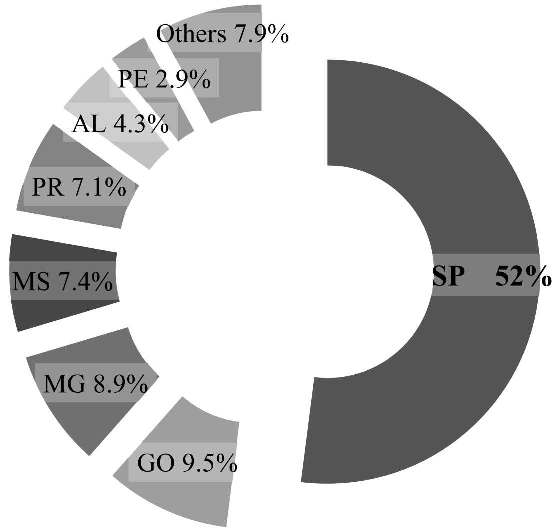
1.2.1. Sugarcane in Brazil

Brazil is one of the major producers of biomass, has great potential to employ and develop techniques for the conversion of biomass into biofuels (LENÇO, 2010). The materials with the most research indication for bioenergy are agricultural residue, produced directly in the field during harvest season; forest residues, and agro-industrial waste (VASCONCELOS et al., 2007). According to Empresa de Pesquisa Energética (2015), the Brazilian energy matrix counts with 39.4% of renewable sources. The sugarcane biomass is the greatest representative with 15.7%, surpassing the hydraulic, which got to 11.5%.

The sugarcane was introduced in Brazil in 1532 by the Portuguese colonizers (CONAB, 2014; UNICA, 2004). The crisis in 1929 reduced the sugar exportation and in 1931, the Brazilian government in an attempt to encourage the consumption, added 5% ethanol to the formula of gasoline (MEYER et al., 2012; UNICA, 2004). In order to reduce dependence on oil and due the low demand for Brazilian sugar in the international market, in 1975, it was created the National Alcohol Program (PROALCOOL) (GOLDEMBERG, COELHO and GUARDABASSI, 2008; MEYER et al, 2012). There was much encouragement in the sector, generating new plants only for the production of ethanol. In the mid-80s, 85% of the cars were only running on ethanol (ANDRIETTA, STECKELBERG and ANDRIETTA, 2006). In 2003, it was launched the first flex-fuel car in Brazil (CONAB, 2010). And today, 90% of vehicle sales are composed by flex-fuel, and anhydrous ethanol already represents 27.5% of the mixture in gasoline (TEIXEIRA, 2014).

The 2015/2016 sugarcane crop is estimated at 590 million ton (UNICA, 2015). The demand for sugarcane coupled with soil, climate and territorial conditions make Brazil the largest producer of sugarcane in the world (CONAB, 2010; TEIXEIRA, 2014). According to data from CONAB (2014) (Fig. 1), the cultivation of sugarcane occupies about 9 million ha, representing 1.06 % of the Brazilian territory, and the state of São Paulo, is the largest holder of this culture, with 4.68 million ha. According to the IBA (2015) data, the occupied area of planted forests in Brazil is 7.74 million ha. Comparing the sugarcane plantations with planted forests, the portion of sugarcane crops outweigh the planted forests by approximately 16%.

Figure 1 - Total area of sugarcane plantations in Brazil.



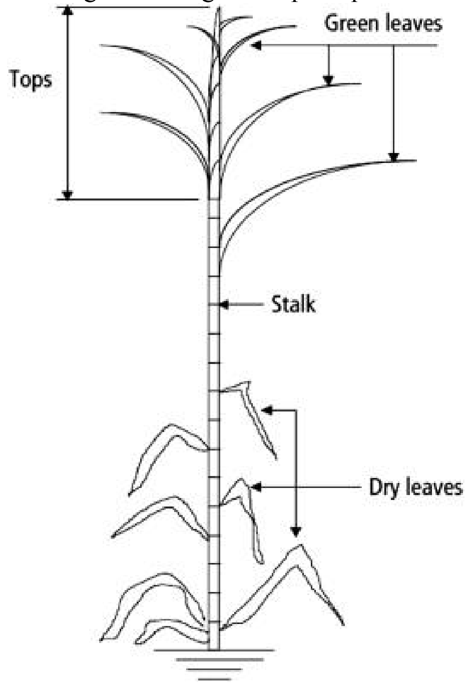
Source: CONAB, 2014

1.2.2. Use of Sugarcane Trash

The sugarcane (*Saccharum* sp.) (Fig.2) is a rigid plant and provides two types of waste: bagasse, which is already being used as a source of energy for their own producers, and the trash (straw and leaves). On its leaves there are spikes, requiring the use of fire to facilitate its management, mainly in non-mechanized areas (LEAL et al., 2013; RIBEIRO and FICARELLI, 2010; RÍPOLI, MOLINA JR and RÍPOLI, 2000).

According to Soccol et al. (2010) the trash and bagasse represent two thirds of the sugarcane biomass. Hassuani, Leal and Macedo (2005) estimated an average generation of 14 $ton.ha^{-1}$ of trash on a dry basis. And Rípoli and Rípoli (2004) define the trash as the "remaining material on the surface plot after harvest, mostly mechanized, made up of green leaves, straw, pointer and/or its stem fractions (industrialized or not); eventually, roots and fractions of soil particles added to them".

Figure 2 - Sugarcane plant parts.



Source: Hassuani, Leal and Macedo, 2005.

The sugarcane pre-harvest without using fire implies higher risks and lower work efficiency, because its burning makes the stem more malleable for cutting (RIBEIRO and FICARELLI, 2010; RÍPOLI, MOLINA JR and RÍPOLI, 2000). However, the burning of the trash, which is an incomplete combustion, emits polluting gases such as NOx, CO, HC and other toxic compounds that cause environmental and health problems for the inhabitants of areas close to sugarcane fields (RIBEIRO and ASSUNÇÃO, 2002; RIBEIRO and FICARELLI, 2010). The use of mechanized harvest increased in the sugarcane plantation in the mid-90s to reduce costs and adapt to current environmental requirements (MUNDIM et al., 2009).

In Brazil, some laws were created to eliminate the use of fire in sugarcane plantations due to the negative consequences generated for society and the environment. The Federal Decree No. 2,661, of July 8, 1998, in Chapter IV, art.16 provides for the gradual elimination of fire in mechanized areas of sugarcane crops (slope less than 12%) and areas larger than 150 ha. The São Paulo State Law 11,241 of September 19^{th}, 2002, provides the gradual elimination of sugarcane straw burning by 2021 for mechanized areas and by 2031 for non-mechanized areas. However, an Agro-environmental Protocol was signed by the major producers of sugarcane, anticipating the total elimination of sugarcane straw burning for 2014 for mechanized areas and 2018 for non-mechanized areas.

On the other hand, Law No. 1,952 of December 20th, 1995, of the city of Paulínia (São Paulo), that prohibits the sugarcane trash burning in its territory, was ruled unconstitutional. In May 2015, the Supreme Court held that there are already laws on the federal and state level, to the use of fire in agricultural areas and the gradual elimination as expressed above, so the municipality could complement such laws and not annulment them.

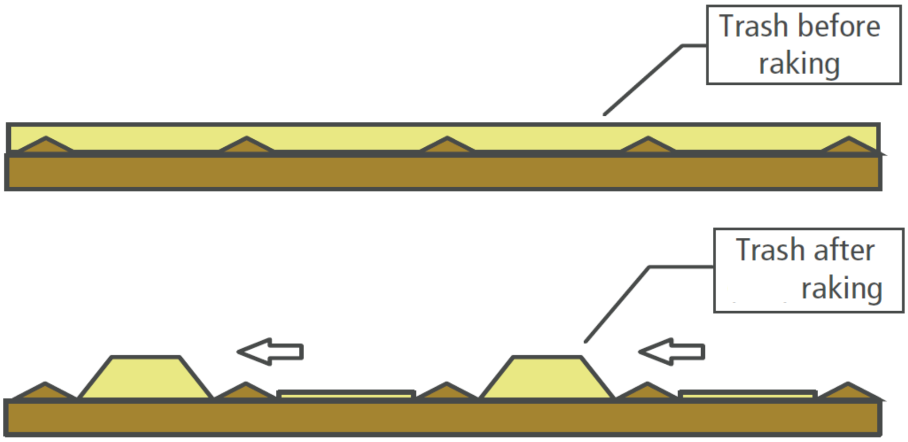
The compliance of the existing laws, there was an increase in the amount of lignocellulosic material left in the field (LEAL et al., 2013). This residue may remain on the ground to improve the physical conditions of the soil, reducing the loss of water and nutrients (SOUZA et al., 2005). However, due to the favorable conditions of the trash coverage, high humidity and low temperature, there is an increase of pests which can cause further damage to the plantation (MUNDIM et al., 2009; RAVANELLI et al., 2011).

The spittlebug (*Mahanarva fimbriolata* (Stål)), which was considered a secondary pest for sugarcane plantation, with trash accumulation in the field has become relevant for this culture (MADALENO et al., 2008; MUNDIM et al., 2009; RAVANELLI et al., 2011). According to Dinardo-Miranda et al. (2004), the spittlebug is a problem because it establishes and reproduces quickly in unburned sugarcane areas. This pest causes negative effects on the productivity of stalks and can also participate in the addition of contaminants that interfere in the sugar production and in the fermentation inhibition. Then, even contributing to the maintenance of nutrients and soil conservation, the trash recovering can lead to problems, raising the management costs of culture.

In order to avoid pesticide cost and others problems in remain the sugarcane trash on the field, a solution would be the mechanized collection of trash, which can be used for energy purposes (LEAL et al., 2013; MUNDIM et al., 2009). Residues of sugarcane have great potential to improve and diversify the Brazilian energy matrix (RÍPOLI, MOLINA JR and RÍPOLI, 2000).

The problem for the use of this biomass in mechanical harvesting is how to recover and make it available in the most appropriate way. To recover the material in bales is necessary to raking (Fig. 3) the trash scattered on the ground (MICHELAZZO and BRAUNBECK, 2004). This system is used by several mills in São Paulo State (RÍPOLI and GAMEIRO, 2007). The process is conducted by the machine called baler where the biomass is collected and densified in bales (MICHELAZZO and BRAUNBECK, 2004).

Figure 3 - Raking scheme.



Source: Hassuani, Leal and Macedo, 2005 (adapted).

The bales can be stored after recovery. The surface of round bale shape plays a role to protect the bale in the outdoor storage. Thus, the inner part of the bale is preserved while the surface is exposed to degradation process (SANDERSON, EGG and WISELOGEL, 1997). The outdoor storage has the advantage of having a lower cost and its location is near the road to facilitate transportation of the biomass (MARTELLI, BENTINI and MONTI, 2015).

1.2.3. Impurities Content of Sugarcane Trash

The recovery of trash increases the mineral impurities because the leaves were scattered on the soil. After transport to the location where it will be processed, the bale will need to be unloaded, unpacked, cleaned and sent for processing (GÓMEZ et al., 2014). According to Braunbeck and Bianchi (1988) cited by Franco (2003), the type of machine, the type of soil and the process used for picking and loading can aggravate the amount of impurities in sugarcane. The mineral impurities contained in the sugarcane trash may also have been influenced by other factors: sugarcane variety, level of exudation, sugarcane cutting system. The equipment used for removing these mineral impurities are not efficient. Excess of impurities affect the material quality (GÓMEZ et al., 2014).

The increase in disposable trash can be used as a supplement to sugarcane bagasse in boilers for energy production (DIAS et al., 2011; LEAL et al., 2013; SEABRA et al., 2010). The bagasse and the trash are different materials with different chemical compositions. The addition of trash to bagasse in the boilers should be performed with caution, as the trash is heterogeneous and has higher amount of impurities than bagasse (RÍO et al., 2015; SEABRA et al., 2010). Some mills use the percentage of no more than 20 to 25% of trash in this mixture with the bagasse (CERQUEIRA-LEITE, 2007).

The amount of mineral impurities influences technical problems in biomass compaction process (GÓMEZ et al., 2014) and also in combustion in boilers, such as "fouling" and "slagging" (JENKINS et al., 1998). The "fouling" occurs when substances vaporized during the combustion are deposited on the surfaces and "slagging" corresponds to deposit of ashes in a form of molten (SEGGIANI, 1999). Biomasses as sugarcane waste has, as main components of the ash content, silica and potassium (BAXTER et al., 1998; CERQUEIRA-LEITE, 2007; LEAL et al., 2013). Several authors also discussed the ash content variation. It was explained by different recovery processes, the variety of sugarcane (BRAUNBECK and BIANCHI, 1988 apud FRANCO, 2003), growth stage (VASSILEV et al., 2010), planting location (VASSILEV et al., 2010), soil type (VASSILEV et al., 2010; BRAUNBECK and BIANCHI, 1988 apud FRANCO, 2003) and sampling errors.

The grinding process of sugarcane bagasse with water can leach mineral impurities improving the quality of the biomass for fuel. For the trash this process becomes infeasible due to high consumption of water and the increase of moisture content with this step (CERQUEIRA-LEITE, 2007).

1.2.4. Chemical Properties of Sugarcane Trash

The characterization of the material is a crucial step to fit and allocate the best purpose for biomass (NAIK et al., 2010; SANTOS et al., 2012; SZCZEBOWSKI et al., 2014; VASSILEV et al., 2010). This characterization will give the possibility to identify properties, quality, applications and environmental problems (VASSILEV et al., 2010). The biofuel characterization can be divided into: physical, chemical, thermal and mineral properties (DEMIRBAS, 2005).

The chemical properties are very important to obtain a quality fuel. Some chemical analyzes are ultimate analysis, proximate analysis and high heating value (HHV) (DEMIRBAS, 2005). The proximate analysis is used to determine the moisture content, volatile matter, fixed carbon and ash content, while the ultimate analysis determines the percentages of the elements, as carbon, hydrogen, nitrogen, oxygen and sulfur of the biomass (GARCÍA et al., 2013, YIN, 2011). These two types of tests are related to the heating value (GARCÍA et al., 2013; PROTÁSSIO et al., 2011; YIN, 2011).

Calorific value is defined as “the heat produced by combustion of a unit quantity of a substance under specific conditions” (AMERICAN SOCIETY FOR TESTING AND MATERIALS, 1998). According to Gómez et al. (2014), “the high heating value (HHV) is the maximum amount of heat produced during the combustion in perfect conditions for its burning in relation to 1 kg of solid or liquid fuel, or 1m^3 of gaseous fuel”. The HHV is probably the feature that best defines biomass as a fuel (GARCÍA et al., 2013). Other elements may influence the HHV, such as lignin content and extractives (TELMO and LOUSADA, 2011).

Cellulose, hemicelluloses, lignin, extractives and minerals are the principal constituents of the biomass (BRAND and MUÑIZ, 2012; OLIVEIRA et al., 2013). The largest portion of carbohydrates in plants is holocellulose that is composed by cellulose and hemicelluloses (SANTOS, 2008; TELMO and LOUSADA, 2011). Lignin is the third most abundant material in the plants. It plays an important role in mechanical strength in vascular plants. And also, lignin is considered a source of bioenergy (SANTOS, 2008). The extractives are organic compounds which can be found in the forms of fats, waxes, alkaloids, proteins, simple and complex phenolics, simple sugars, pectins, mucilages, gums, resins, terpenes, starches, glycosides, saponins, and essential oils (PETTERSEN, 1984). According to Santos et al. (2012), sugarcane trash is formed by about 40% of cellulose, 30% hemicelluloses, 25% lignin and 5% of extractives.

1.2.5. Sugarcane Trash for Energy Purposes

It is estimated an average generation of 14 ton.ha^{-1} of sugarcane trash on a dry basis (HASSUANI, LEAL and MACEDO, 2005). As a result of sugarcane trash accumulation, the mills have tried to burn this trash with bagasse for power generation (CERQUEIRA-LEITE, 2007). However, this biomass presents low density making it disadvantageous (NAKASHIMA et al., 2014). A study of sugarcane trash briquettes shows that the density in briquette form is around 16 times greater than its density *in natura* (SILVA et al., 2015).

Biomasses in general, such as agricultural waste, wood, sawdust, and other materials can be briquetted (BHATTACHARYA et al., 1989; TRIPATHI, IYER and KANDPAL, 1998). Briquetting is a densification process of the raw material, with heterogeneous characteristic transforming it into a homogeneous and uniform product. Its main advantages are low moisture content, the uniform size and quality fuel. The increase of heating value per unit volume creates an alternative fuel to charcoal. The briquettes are easy to transport, storage and handling (BHATTACHARYA et al., 1989).

The variables in briquettes production are moisture content (RHÉN et al., 2005; TRIPATHI, IYER and KANDPAL, 1998), higroscopicity (YAMAJI et al., 2013) and particle size (GONÇALVES et al., 2013; NAKASHIMA et al., 2014; SILVA et al., 2015; TRIPATHI, IYER and KANDPAL, 1998). Some properties for high quality briquettes are low ash content, low volumetric variation and good mechanical strength (BRASIL et al., 2015). Silva et al. (2015) in their study of briquettes concluded that the production of sugarcane trash briquettes is technically feasible.

CHAPTER 2 – INFLUENCE OF STORAGE TIME AND PARTICLE SIZE IN THE CHARACTERIZATION OF SUGARCANE TRASH

2.1. INTRODUCTION

The planted area of sugarcane in Brazil was 9,0 million ha in 2014 (CONAB, 2014). And it was estimated an average generation of 14 $ton.ha^{-1}$ of trash (top and leaves) (HASSUANI, LEAL AND MACEDO, 2005). According to Leal et al. (2013), the two most promising uses for sugarcane trash are the fuel for the generation of energy or feedstock for biofuel of second generation. The use of trash makes the possibility to increase the use of renewable energy in the country energy matrix (RÍPOLI, MOLINA JR and RÍPOLI, 2000).

The use of this trash for energy purposes requires an adequate recovery from the field (LEAL et al., 2013; RÍPOLI and GAMEIRA, 2007). An alternative to the recover the trash would be the combination of raking and baling. The raker is the accumulation of trash to feed the balers (Fig.4). This is a process that must be done with high efficiency because it can significantly affect the raking and other operations due to mineral impurities (GÓMEZ et al., 2014). Afterwards, the material recovered is used to form the balers (Fig.4).

Figure 4 – (a) Raker; (b) Baler; (c) Sugarcane trash bale.

Source: author

Depending on the performance of the raking operations, the amount of soil contaminants can adversely affect the material, resulting in higher ash content. The ashes can be the result of the material itself and/or from contaminants. The ashes are formed mainly by inorganic substances which do not burn at the end of the combustion process (BRAND, 2010). Gómez et al. (2014) and Jenkins et al. (1998) pointed out some difficulties presented by inorganic materials in ashes: they can form encrustation on boiler and abrading the equipment for biomass densification. Therefore, the proximate analysis that comprises the ash, volatile, fixed carbon and moisture content test is the key to understanding the thermal behavior of the material (GARCÍA et al., 2013).

Biomass is a heterogeneous material. This characteristic can cause sampling errors, especially when the samples required for the equipment are in low quantity (eg. less than 1g for ash content analysis). It is possible to notice the differences when particles of that material are separated in larger and lower particle sizes (BRIDGEMAN et al., 2007).

The aim of this study was to verify the influence of storage time and particle size on the characterization of sugarcane trash.

2.2. MATERIAL AND METHODS

2.2.1. Material

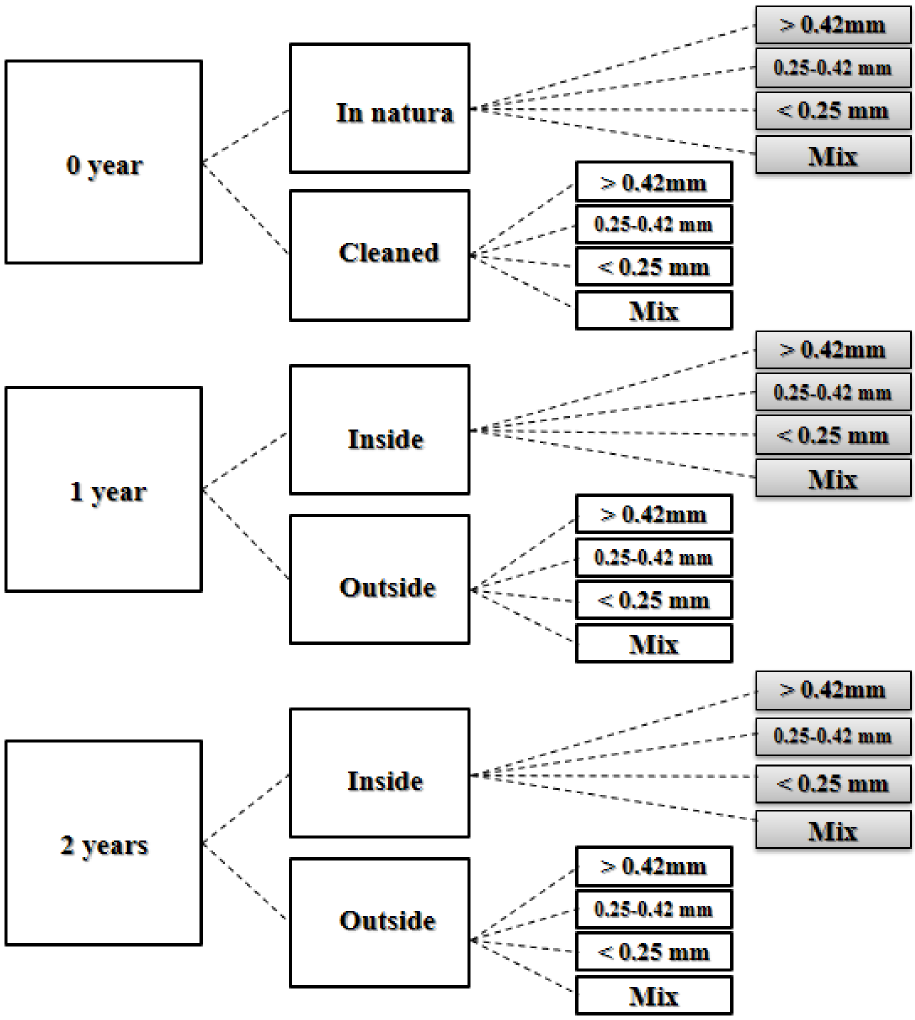
The sugarcane trash used in this study was collected at ‘Fazenda Corredeira’, located in the municipality of Ibaté (21.9547°S, 47.9967°W) in São Paulo State. The farm has a planted area of 800 ha with an average yield of 87 $ton.ha^{-1}.year^{-1}$. The sugarcane varieties planted are RB 855453, RB 867515, RB 855536, SP 803280, SP 813250.

The samples were collected directly from the bales stored on the field. Samples from the surface (outside) and the inner (inside) of different bales were collected. The purpose was to evaluate the surrounding (soil, rain, wind) effects on the bales and the variation of storage time the sugarcane straw. The storage time was 0, 1 and 2 years. To verify the influence of contaminants in the material it was used samples of 0 year treatment. They were taken in natural form, washed in running water and dried in oven. The analysis of contaminants is important due to the extreme abrasion of molds and pistons in the briquetting process of sugarcane trash.

The treatments were divided according to the particles size. They were used particle > 0.420mm, 0.250-0.420mm, < 0.250mm. And fourth treatment was made by the sample without separation of particle size ("mix"). The treatments were based on 3 storage time (0, 1 and 2 years), 2 bales portion (outside and inside), 4 particle size (particle > 0.420mm, 0.250-0.420mm, < 0.250mm and fraction mix) and cleaning treatment for 0 year (with and without) in a total of 24 treatments (Fig.5).

The sugarcane trash was oven dried, crushed using a vertical rotor mill with fixed and mobile knives Willey MA -340.

Figure 5: Treatments plan of the study.



Source: Author.

2.2.2. Particle Size Distribution

All the different storage time of sugarcane trash were analyzed for particle size distribution. The sieves used were 12.70mm (1/2in), 6.35mm (1/4in), 4.00mm (5 mesh), 2.00mm (10 mesh), 0.841mm (20 mesh) for sugarcane trash before the grinding. And the sieves used for sugarcane trash after the grinding were 0.420mm (40 mesh), 0.250mm (60 mesh) and 0.149mm (100 mesh). The material went through a separation process in an orbital shaker with these sieves and intermittent shaking action, type Marconi – MA 750.

2.2.3. Proximate Analysis

Proximate analysis was provided with samples at 0% moisture content, with 3 repetitions for each treatment. The ash content was based on the American Society for Testing and Materials (ASTM) D1102-84 standard. Approximately 1.0g of the sample was placed in a porcelain crucible and brought to a temperature of 600°C in the muffle furnace for 6 hours. For its cooling, the crucible was placed in a desiccator until it reached room temperature and it was weighted.

The volatile content was based on American Society for Testing and Materials (ASTM) E872-82. In porcelain crucible with cover, it was placed about 1.0 g of sugarcane trash. The crucible with the lid and the sample was left in the muffle furnace at 900°C. The first 3 minutes with the oven door opened, and then closed, standing for 7 minutes. The crucible was placed in a desiccator to be weighed after reached room temperature.

Fixed carbon was obtained by the following equation (1):

$$\%fixed\ carbon = 100 - (\%ash\ content + \%volatile\ matter) \quad (1)$$

2.2.4. Chemical Composition of Ash Content

The chemical composition of sugarcane trash ashes for 0 year (without cleaning) and 0 year cleaned was determined by X-ray fluorescence (WDXRF) in Rigaku Supermini 200. The samples (0% moisture content) were prepared in the mold filled with boric acid and ashes from sugarcane trash. It was used a hydraulic press (20 ton) to produce the tablet (densification). The tablet was placed in the sample holder and analyzed with a resolution of 26eV.

2.2.5. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analyzer (EDXA)

The morphology of sugarcane trash was analyzed by scanning electron microscopy (SEM). Samples were placed on an aluminum base and fixed in a carbon tape. Prepared samples were kept in a desiccator until the time of analysis. To obtain the images was used scanning electron microscopy Hitachi TM3000 operated with an acceleration voltage of 15 kV with Energy Dispersive X-ray Analyzer (EDXA).

2.2.6. High Heating Value (HHV)

The high heating value (HHV) was obtained based on standard American Society for Testing and Materials (ASTM) D5865-98, using a calorimeter bomb IKA Model C200 with isoperibol method.

2.2.7. Statistical Analysis

The proximate analysis and the HHV were statistically evaluated by analysis of variance (ANOVA). The Tukey test was applied at 5% significance level for treatments that showed significant differences. All statistical analyzes were performed by R 2.11.1 software. (R STUDIO, 2012; R DEVELOPMENT CORE TEAM, 2008).

2.3. RESULTS AND DISCUSSION

2.3.1. Particle Size Distribution

The particle size distribution of sugarcane trash storage treatments before grinding is showed in Fig. 6 and the distribution after grinding in Fig. 7.

Figure 6 – Particle size distribution of sugarcane trash before grinding.

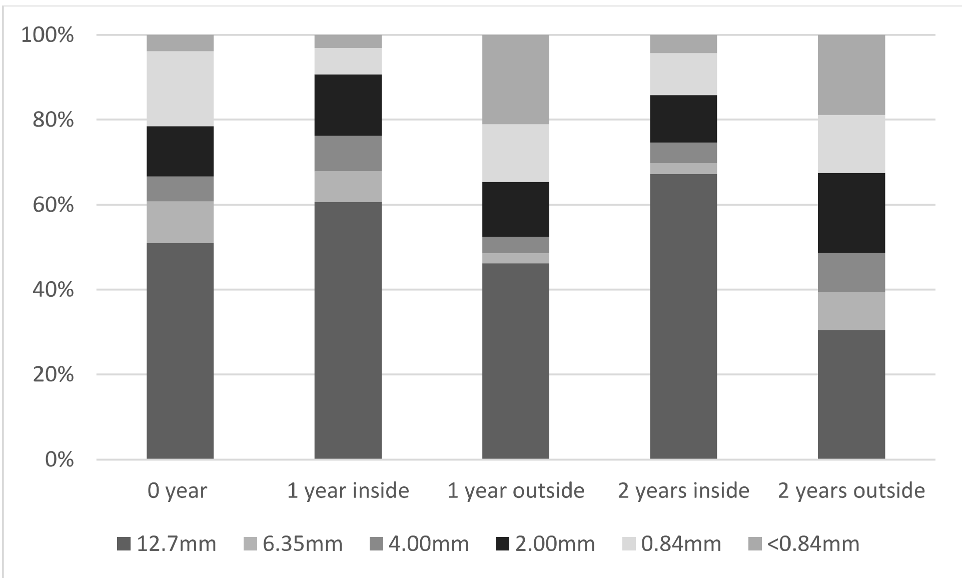
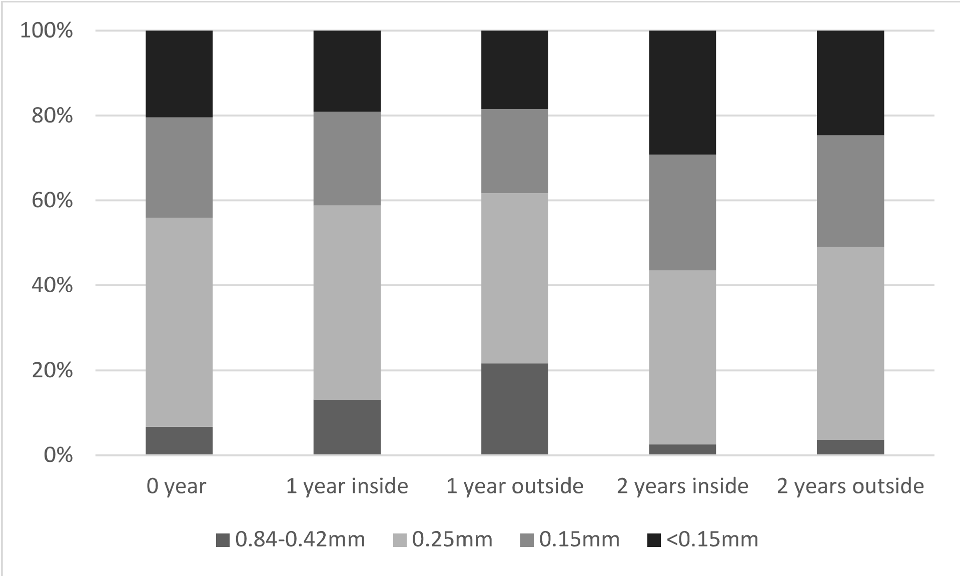


Figure 7 – Particle size distribution of sugarcane trash after grinding.



Before grinding, the highest percentage was retained in the sieve of 12.7mm (½ inch), ranging from 30.5 a 67.3%. This particle size is not allowed to briquettes production in laboratory scale. The distribution after grinding presented the higher retention in 0.25 mm (60 mesh) sieve, ranging from 39.75% to 49.01%.

The particles distribution of sugarcane trash before grinding (Fig. 6) has a wider range in particle sizes if compared to the distribution after grinding. This particles wide distribution gives a heterogeneous characteristic to the material and it can difficult the briquettes formation. After grinding, the distribution became narrow (Fig. 7). And the material is more homogeneous with this distribution. It is known that particle size is an important variable that interferes in briquetting process (SILVA et al., 2015). However, the grinding process must to be studied carefully in industrial scale due to the high cost.

The sugarcane trash with 2 years storage time after grinding showed higher amounts of particles retained in sieves 0.149mm and < 0.149mm (100 mesh) compared to other storage time. This behavior might be due to degradation of the material in their storage, making the material more breakable (LEHTIKANGAS, 2001).

2.3.2. Proximate Analysis and High Heating Value (HHV)

The results for proximate analysis and the HHV for different storage time and particle size are found in Table 1 and Table 2. The standards used for ash content analysis, such as American Society for Testing and Materials (ASTM) D1102 and Technical Association of Pulp and Paper Industry (TAPPI) T211om-02 specify that the sample should be less than 40 mesh particle size (0.420 mm). It is known that biomass is a heterogeneous material. And it is difficult to represent it in just 1.0g of material. To verify the variation in the material among different particles size, the analysis was divided in 4 classes: > 0.420mm, 0.250-0.420mm, < 0.250mm and mix.

Table 1- Proximate analysis of different size fractions of sugarcane straw.

Analysis	Storage	> 0.42mm			0.42-0.25mm			< 0.25mm			Mix		
Ash content (%)	0 year	4.63±0.26	a	D	5.29±0.07	a	C	12.29±0.16	a	A	6.29±0.30	b	B
	0 year cleaned	3.65±0.05	b	B	3.75±0.05	c	B	6.78±0.49	c	A	4.00±0.06	c	B
	1 year inside	2.16±0.15	d	C	4.03±0.05	bc	B	12.38±0.16	a	A	4.00±0.17	c	B
	1 year outside	2,41±0.04	cd	D	5.44±0.68	a	C	12.72±0.27	a	A	9.43±0.78	a	B
	2 years inside	3.38±0.20	b	C	4.70±0.32	ab	B	8.34±0.05	b	A	4.90±0.18	c	B
	2 years outside	2.70±0.10	c	B	2.83±0.10	d	B	6.49±0.05	c	A	6.14±0.28	b	A
Volatile matter (%)	0 year	77.22±1.04	c	A	77.23±1.17	cd	A	72.97±0.60	bc	A	77.50±0.20	c	A
	0 year cleaned	79.62±0.15	b	B	82.59±0.20	a	A	75.76±1.68	a	C	79.50±0.61	ab	B
	1 year inside	81.09±0.60	a	A	79.73±0.25	b	B	72.35±0.36	c	C	79.91±0.63	a	AB
	1 year outside	81.00±0.27	ab	A	76.11±0.98	d	B	68.30±0.93	d	C	75.15±0.78	d	B
	2 years inside	79.97±0.10	ab	A	78.38±0.04	bc	B	75.12±0.34	ab	C	78.43±0.40	bc	B
	2 years outside	79.83±0.14	ab	A	79.44±0.14	b	A	77.05±0.15	a	B	77.43±0.16	c	B
Fixed Carbon (%)	0 year	18.14±1.14	a	A	17.47±1.19	ab	A	10.47±1.01	d	B	16.21±0.45	ab	A
	0 year cleaned	16.72±0.20	ab	A	13.65±0.19	c	B	17.46±1.19	ab	A	16.50±0.55	ab	A
	1 year inside	16.74±0.46	ab	A	16.23±0.22	b	AB	15.27±0.20	c	B	16.08±0.65	ab	AB
	1 year outside	16.60±0.26	b	B	18.44±0.39	a	A	18.98±0.66	a	A	15.41±0.09	b	BC
	2 years inside	16.65±0.13	b	A	16.90±0.33	b	A	16.53±0.37	bc	A	16.66±0.21	a	A
	2 years outside	17.46±0.11	ab	A	17.33±0.23	ab	A	16.45±0.20	bc	B	16.43±0.25	ab	B

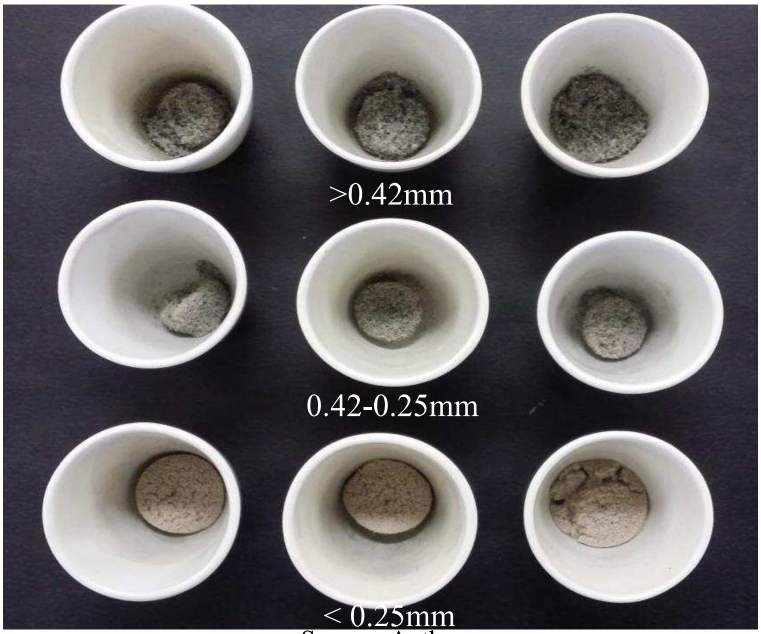
*The averages followed by the same letter (lower case) in the column and the same letter (capital letter) in the line do not differ statistically by Tukey test at 5% significance level.

In Table 1 it can be noted that there is a tendency to increase the amount of ashes in all treatments while the particle size decreases. Bridgeman et al. (2007) observed the same behavior for reed canary grass and switchgrass. The ash content of the smaller size particles (<0.088mm) fraction was approximately twice that of the larger particles (>0.088mm) treatments. It is likely the mineral impurities are concentrated in fine particles. Tamaki and Mazza (2010) analyzed various agricultural residues (triticale, wheat, barley, oat and flax). The material was separated into fine (<0.177mm), medium (0.841-0.177mm), and coarse

(>0.841mm) fractions. The average ash measurement (6.1%) of the fine fraction was five to eight times higher than the other fractions (medium, 1.2%; coarse, 0.8%). The ash content for flax (27.7%) in the fine fraction (<0.177mm) were more than 10 times higher than in the fraction >0.841mm (2.2%).

The ash content values obtained in this study ranged from 2 to 12% among all treatments (Fig. 8). The ash content found for the sugarcane trash is very high compared to the commonly biomass used for briquetting processes. According to Demirbas (2000) the wood biomass has an average of 0.5% of ash content. The composition itself of the leaves in the sugarcane presents silica, which indicates that the inorganic material obtained are from the plant itself and some contaminants from the soil. Gómez et al. (2014), Demirbas (2005), Jenkins et al. (1998) claimed that the ash could cause wear and corrosion to equipment. Gómez et al. (2014) obtained for ash content of sugarcane straw 7.5%, for green leaves 2.1% and for sugarcane trash 2.2%. Hassuani, Leal and Macedo (2005) and Peláez Samaniego (2007) presented for sugarcane straw 8.15% and 11.7% of ash content, respectively. Szczerbowski et al. (2014) found for the sugarcane straw 6.23% of ash content however the samples used were submitted through a clean process.

Figure 8 - Ash content obtained from sugarcane trash from different particle sizes.

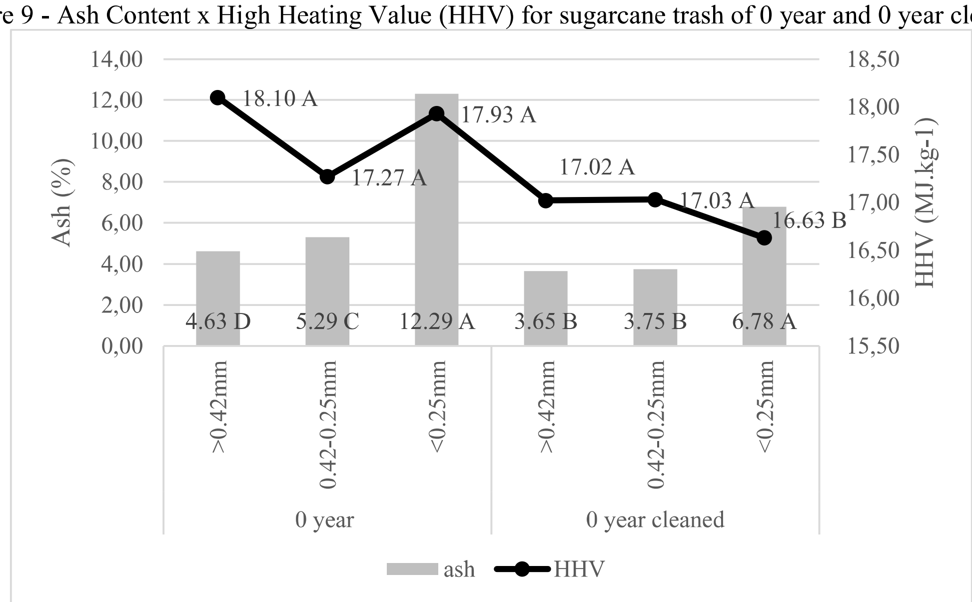


Source: Author

The cleaning process was applied for the treatment 0 year. It was expected that there would be no difference between the particle size treatments. The results showed that the fraction <0.25mm was statistically different from the other particle sizes. This result confirms that mineral impurities still retained in smaller particles even after cleaning in running water.

The treatment 0 year cleaned presented lower percentage of ash content compared to treatment 0 year (without cleaning). The reduction was 21% to >0.42mm fraction, 30% to 0.42-0.25mm fraction, 45% to <0.25mm fraction and 36% to mix. It is necessary to take care when wash the sugarcane leaves prior testing, because the silica on the leaf surface is lost and it can influence the final result (SZCZERBOWSKI et al., 2014). The ash content reduction by cleaning process did not influence the values for HHV (Fig. 9) and showed no statistical difference among treatments for HHV, except for <0.25mm in 0 year cleaned.

Figure 9 - Ash Content x High Heating Value (HHV) for sugarcane trash of 0 year and 0 year cleaned.



*The averages followed by the same letter do not differ statistically by Tukey test at 5% significance level.

The mineral impurities are observed in large amount in the fraction <0.25mm. This fraction is considered the most critical. It was selected the fraction <0.25mm to analyze the effect of storage time on ash content. It was found a reduction of 32% in the ash for treatment 2 years inside compared to 1 year. In the treatment 1 year outside compared to 2 years outside, the reduction was 49% for 2 years. The reduction in ash content was higher in 2 years storage time in the bale surface, probably due to the longer exposure to external factors such as rain and wind. Mos et al. (2013) verified the reduction of mineral impurities during the storage time and associated with senescence and direct contact with rain.

The mix treatment can be used to understand the behavior of all material. The ash content for mix treatment is a result of weighted average of the fractions (particle size distribution). The results for ash content and volatile matter for mix treatment are lower than treatment <0.25mm and higher than treatment >0.42mm and treatment 0.42-0.25mm. It confirms the influence of the particle size distribution on analyzes.

The volatile matter is the amount of material that volatilizes during combustion and represents the largest percentage of the material (BRAND, 2010). The Table 1 shows that volatile matter varied from 68.3% to 82.6%. Hassuani, Leal and Macedo (2005) obtained the results for volatile of dry leaves and the top of sugarcane, 84.5% and 79.3%, respectively. Peláez Samaniego (2007) presented for volatile matter of sugarcane trash 81.55%.

The volatile material plays an important role in the combustion and makes the ignitability easy. From this point of view, volatile matter acts as a promoter in combustion. The burning of volatile is generally quite rapid and follows as fast as volatiles are released (JENKINS et al., 1998; LU et al., 1997).

Heating value is the most important parameter to have a high quality fuel. The heating value are functions of the initial composition (physicochemical, moisture content) of the biomass (RAVEENDRAN and GANESH, 1996), ash content (PROTÁSSIO et al., 2011), extractives (TELMO and LOUSADA, 2011) and lignin (TELMO and LOUSADA, 2011). Hassuani, Leal and Macedo (2005) found for sugarcane dry leaves 17.4 $MJ.kg^{-1}$ and for sugarcane top 16.4 $MJ.kg^{-1}$. Peláez Samaniego (2007) obtained 17.74 $MJ.kg^{-1}$ for HHV of sugarcane trash. The values of HHV found in this work are in Table 2.

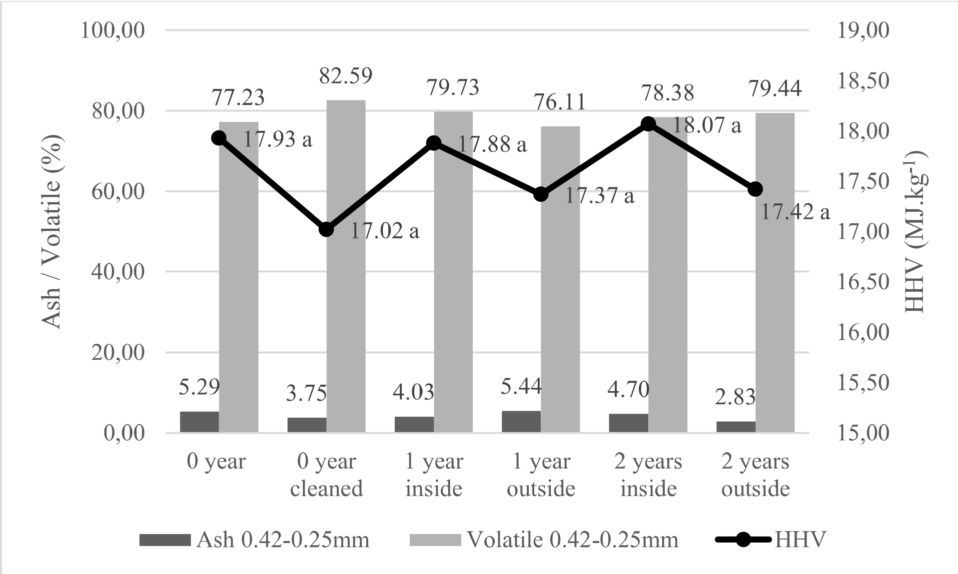
Table 2 - High heating value (HHV) of different size fractions of sugarcane straw.

	Storage	> 0.42mm			0.42-0.25mm			0.25mm		
HHV (MJ.kg-1)	0 year	18.10±0.87	a	A	17.93±0.20	a	A	17.03±0.28	A	A
	0 year cleaned	17.27±0.14	a	A	17.02±0.04	a	A	16.63±0.11	A	B
	1 year inside	18.13±0.40	a	A	17.88±0.73	a	A	17.15±0.94	A	A
	1 year outside	18.32±0.54	a	A	17.37±0.92	a	A	15.93±1.99	A	A
	2 years inside	17.83±0.14	a	A	18.07±0.46	a	A	17.27±0.38	A	A
	2 years outside	17.43±0.53	a	A	17.42±0.32	a	A	17.21±0.16	A	A

*The averages followed by the same letter (lower case) in the column and the same letter (capital letter) in the line do not differ statistically by Tukey test at 5% significance level.

Usually, ash and volatile content are inversely proportional and can influence the results of heating value (BRAND, 2010). The Fig.10 shows the results of ash content, volatile matter and high heating value.

Figure 10- Ash content (%) x Volatile matter (%) x HHV (MJ.kg-1) of 0.42-0.25mm size fraction of sugarcane trash. The averages followed by the same letter do not differ statistically by Tukey test at 5% significance level.

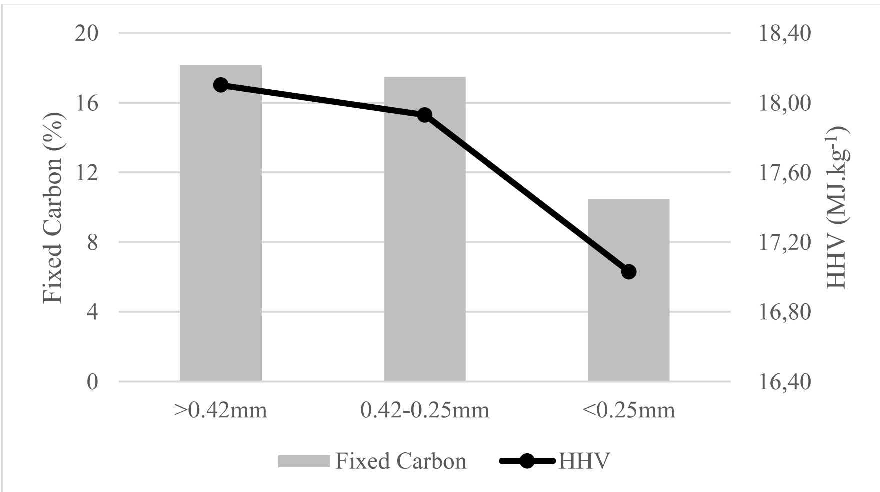


*The averages followed by the same letter do not differ statistically by Tukey test at 5% significance level.

The results showed that there are no statistical differences among the treatments. The difference in ash (maximum of 2.61%) and volatile content (maximum of 6.48%) showed in Tab. 1 was not enough to influence the HHV

It is observed in Fig. 11, a proportional relationship between Fixed Carbon (FC) and HHV.

Figure 11 – Fixed Carbon (%) x High Heating Value (MJ.kg^{-1}) of 0 year sugarcane trash.



The fixed carbon is a fuel material, because it is the fraction that remains after the removal of volatiles and ashes (BRAND, 2010). The result showed that an increase of 7.67% in FC represented a gain of 6.3% in HHV. It confirms the influence of FC on HHV.

2.3.3. Chemical Composition of Ash Content

Inorganic elements can be divided into two types, the elements that are inherent in the biomass composition: calcium, potassium, magnesium, phosphorus, sodium, iron, silicon, zinc and other minerals. The other type are the elements that can also be the result of soil contamination acquired during the biomass collection process (JENKINS et al., 1998; YAMAN, 2003). These inorganic elements can cause "fouling" and "slagging" in equipment (Fig. 12 (a) and (b)), whether in grinding, densification or burning processes for energy.

Figure 12 - (a) Frayed piston of a briquetting machine; (b) Cylindrical molds for briquetting machine; (c) Not uniform briquettes; (d) Briquettes of sugarcane trash.

Source: author.

The inorganic content in ashes of the treatment 0 year (without cleaning) and 0 year cleaned is in Tab. 3.

Table 3 - X-ray Fluorescence (WDXRF) analysis of sugarcane trash inorganic compounds for ashes of 0 year and 0 year cleaned.

Oxide (wt%)		
Type	0 year	0 year cleaned
Na_2O	0.94	1.70
MgO	3.75	5.43
Al_2O_3	**6.76**	**3.85**
SiO_2	**52.37**	**45.93**
P_2O_5	2.14	4.49
SO_3	3.60	3.59
Cl	0.47	1.01
K_2O	10.01	13.58
CaO	10.82	15.83
TiO_2	1.15	0.36
MnO	0.32	0.41
Fe_2O_3	**7.49**	**3.53**
CuO	0.01	0.02
ZnO	0.03	0.08
Rb_2O	0.04	0.05
SrO	0.09	0.13

The amount of inorganic such as silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3) showed a reduction in the treatments 0 year and 0 year cleaned. This may have occurred as they refer to elements that are not from the plant but from the soil. According to Townsend (1982) cited by Loganathan (1987), the elemental composition of some studied soils have approximately 45% silica, 25% alumina and 15% iron oxide.

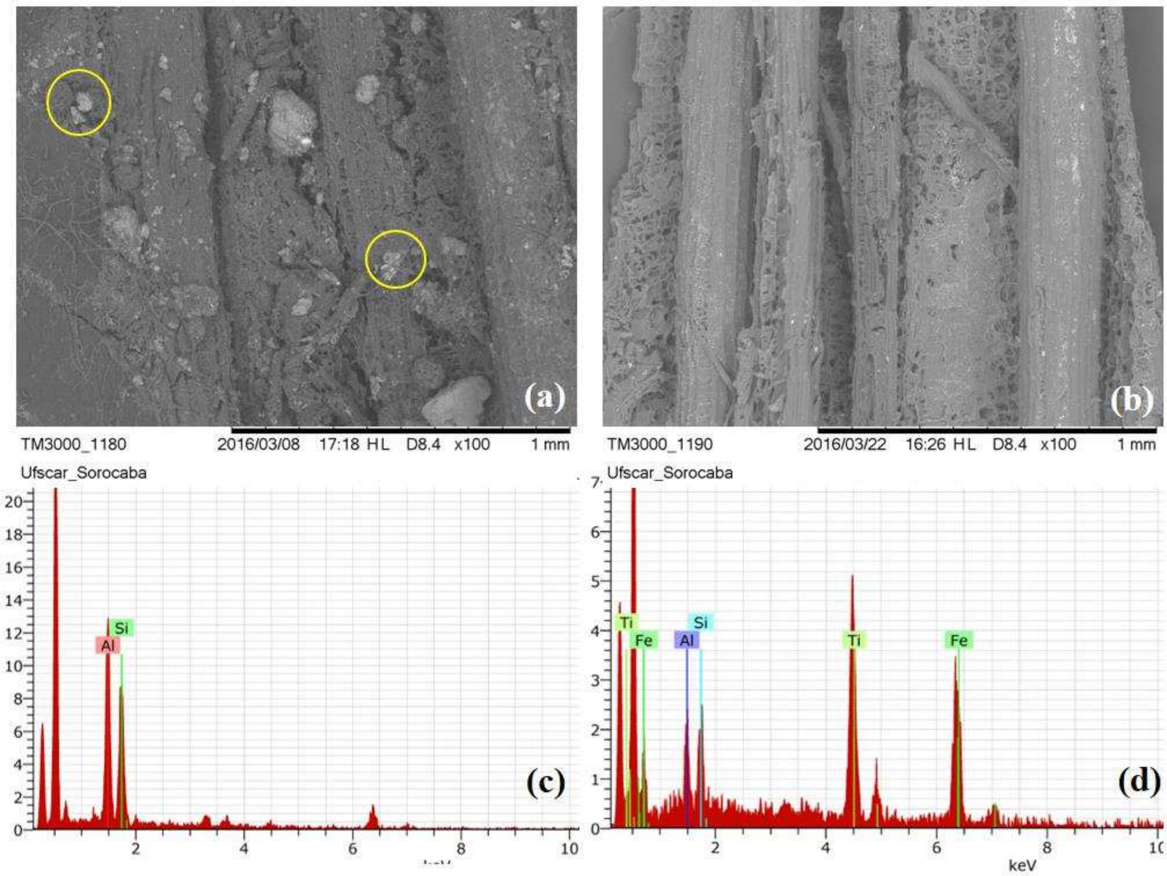
Szczerbowski et al. (2014) obtained 51% of silica in their ash content of sugarcane straw and for bagasse, the amount was about 30%. Peláez Samaniego (2007) the ash chemical analysis for sugarcane straw presented 52.62% of silica, 15.8% of alumina, 3.93% of iron oxide. In this study, silica represented 52.37% of the treatment without cleaning and 45.93% of the cleaning treatment of the total amount of the ashes. This cleaning process in running water decreased 12.3% silica in the ash. The reduction in alumina was 57% and the reduction in iron oxide was 47.1%.

2.3.4. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analyzer (EDXA)

The analysis by Scanning Electronic Microscopy (SEM) was performed for samples of the sugarcane leaf surface before and after cleaning (Fig. 13-21).

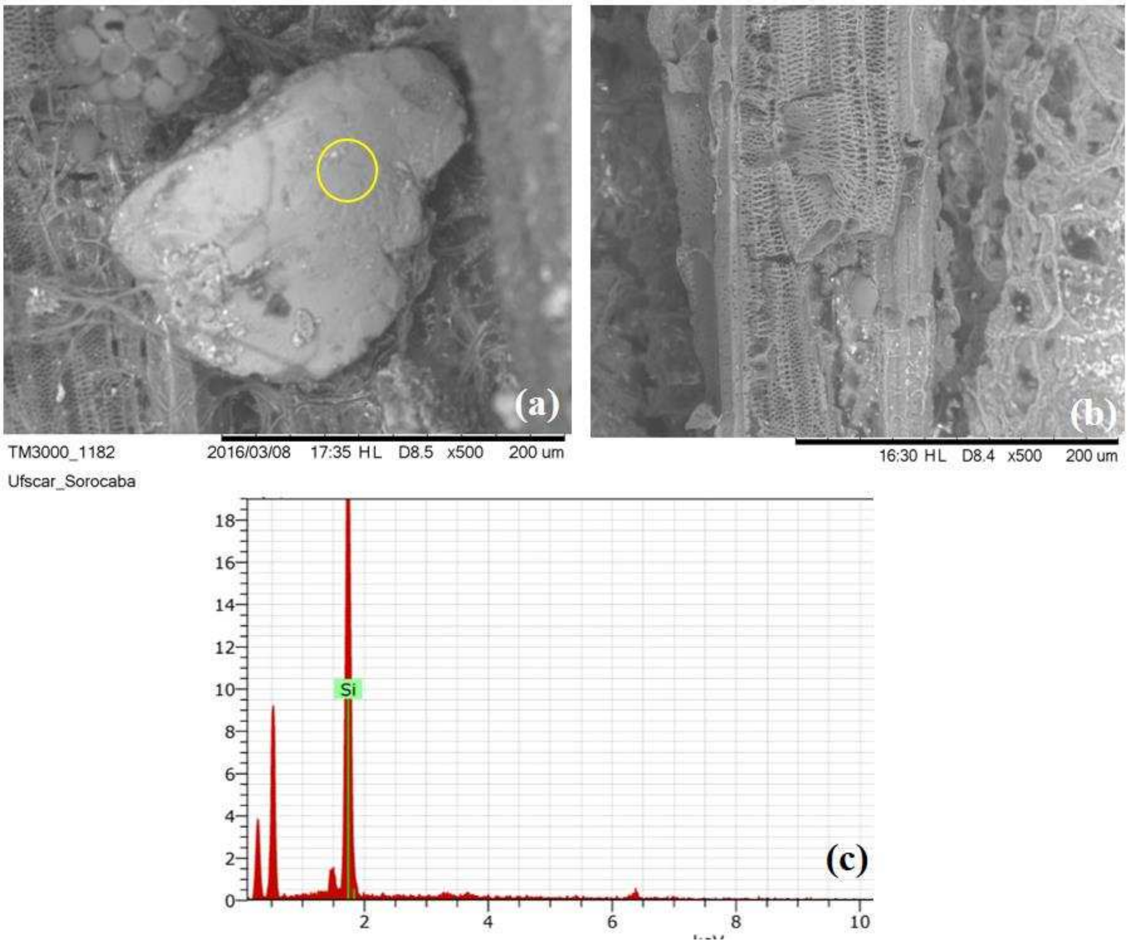
The SEM images show how the cleaning process reduced the amount of impurities on the surface of sugarcane trash. The Fig. 13 (a) examined by EDXA presented on its surface the elements silica, aluminum and iron. In Fig. 14 (a) it was detected a sand grains (silica). In Fig. 15(a) it is shown the contamination by dust (aluminum, iron and silica) and in Fig. 15 (b) still had residual impurities after cleaning. The Fig. 16 presented the elements iron, aluminum, phosphorus and silica.

Figure 13 - SEM images of the sample surface of sugarcane leaf amplified 100 times: (a) before the cleaning process; (b) after the cleaning process; (c) and (d) EDXA results for image (a).



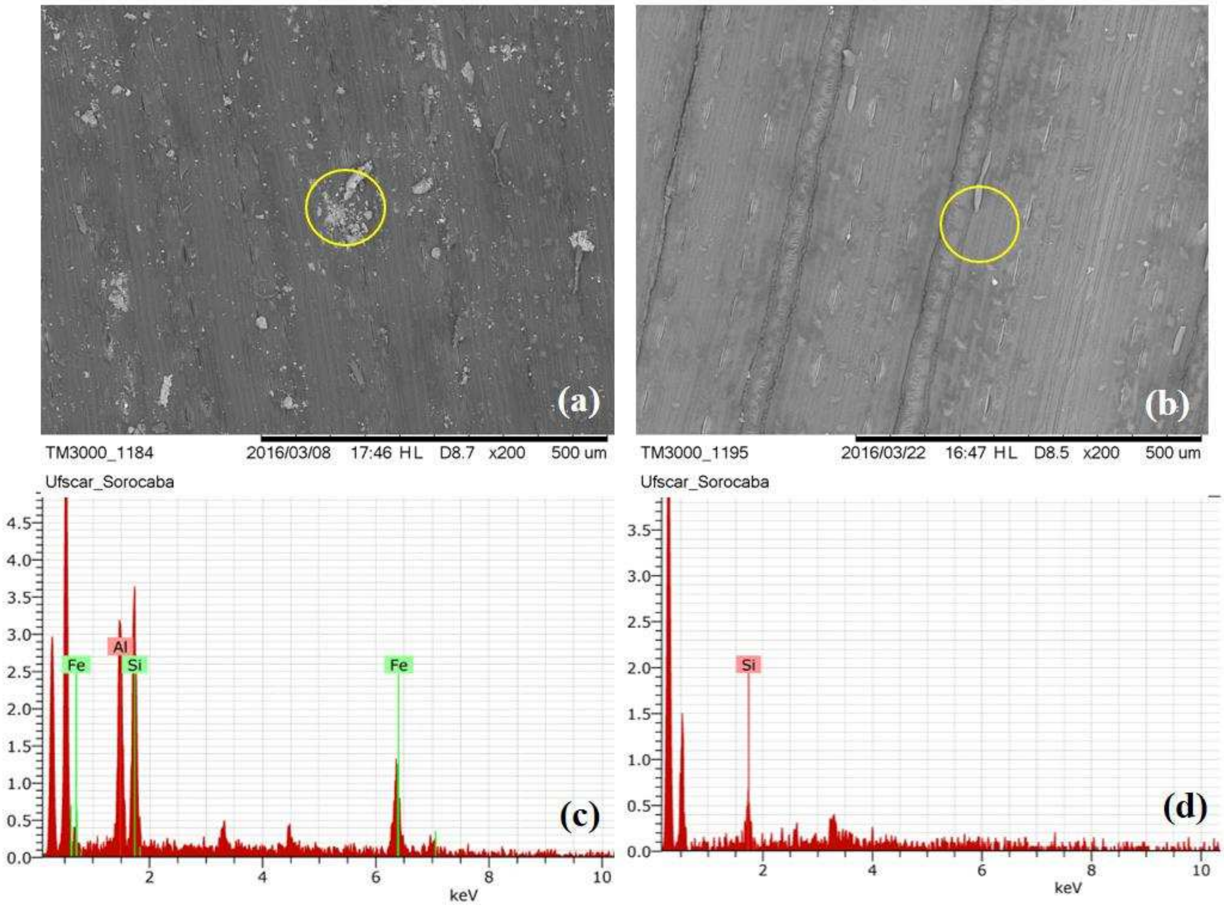
Source: author.

Figure 14 - SEM images of the sample surface of sugarcane leaf amplified 500 times: (a) before the cleaning process; (b) after the cleaning process; (c) EDXA result for image (a).



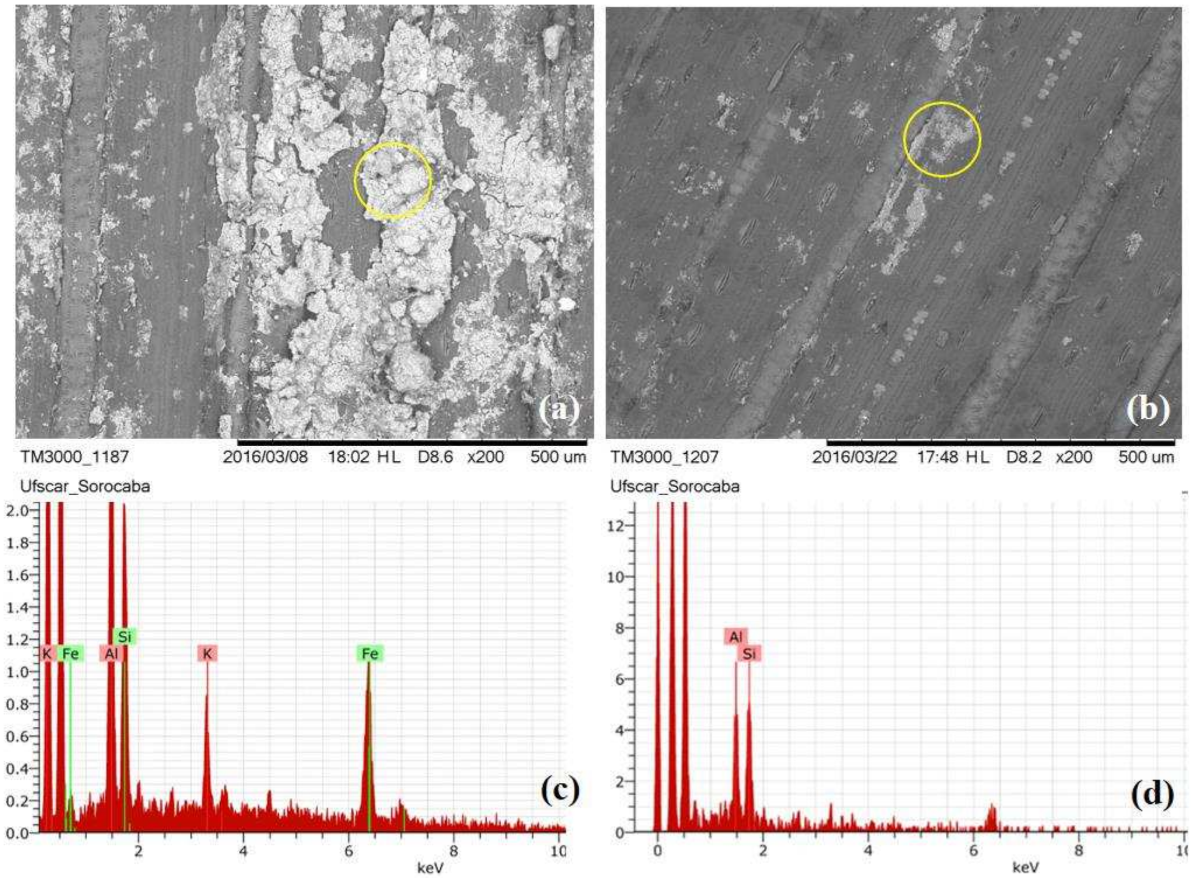
Source: author.

Figure 15 - SEM images of the sample surface of sugarcane leaf amplified 200 times: (a) before the cleaning process; (b) after the cleaning process; (c) EDXA result for image (a); (d) EDXA result for image (b).



Source: author.

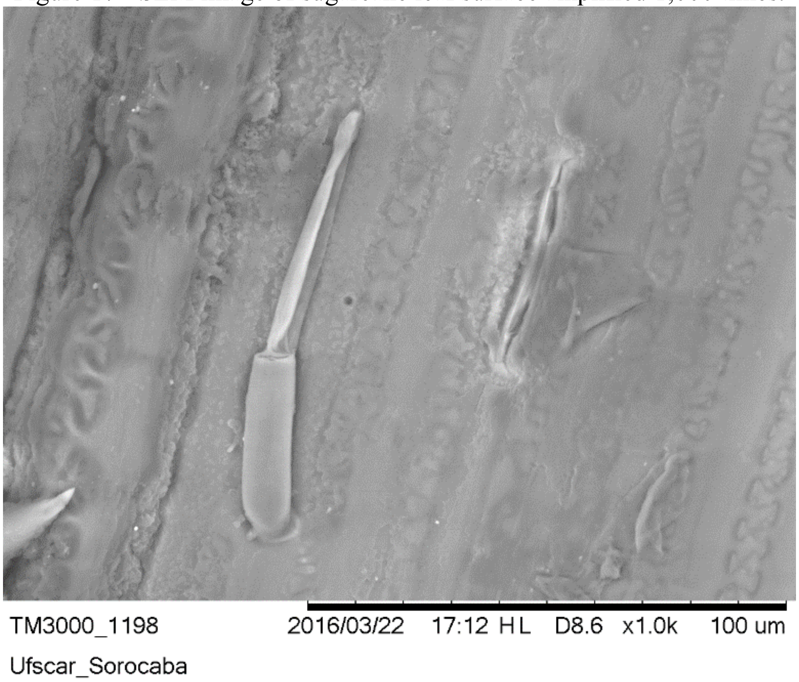
Figure 16 - SEM images of the sample surface of sugarcane leaf amplified 200 times: (a) before the cleaning process; (b) after the cleaning process; (c) EDXA result for image (a); (d) EDXA result for image (b).



Source: author.

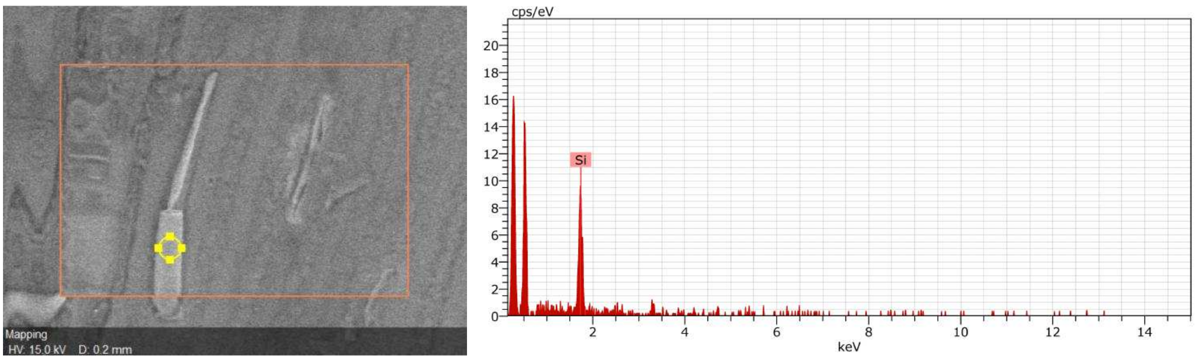
Other elements of the sugarcane leaf itself have a high silica content as detected EDXA (Fig. 17-21). Silica is an element that is part of the composition of the sugarcane leaves (GÓMEZ et al. 2014; KORNDORFER and LEPSCH, 2001; SZCZERBOWSKI et al., 2014). According to Hassuani, Leal and Macedo (2005) it is common for fast-growing grasses, as sugarcane, show high concentrations of silica that act in maintaining their structure.

Figure 17 - SEM image of sugarcane leaf surface amplified 1,000 times.



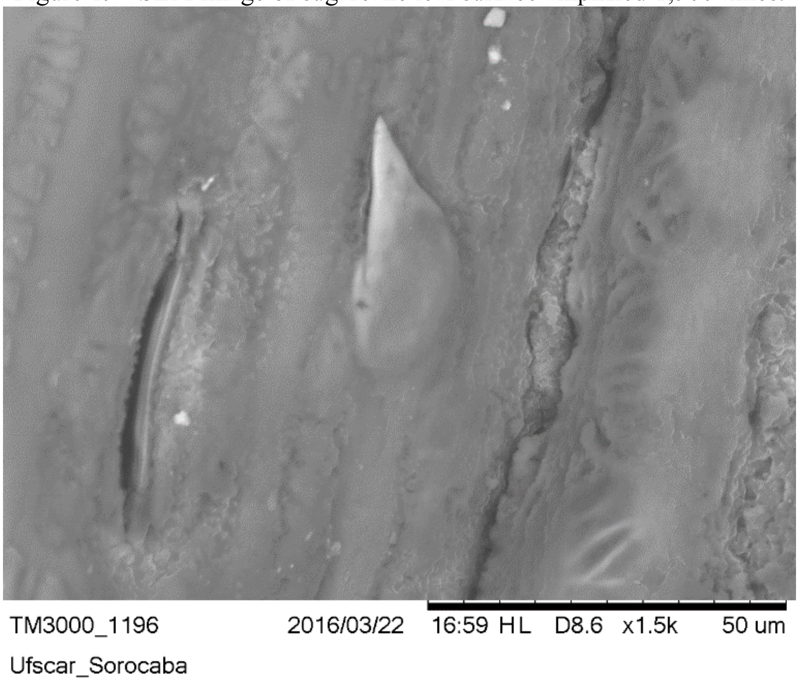
Source: author.

Figure 18 – SEM image for the structure of surface sugarcane trash amplified 1,000 times and the result of EDXA.



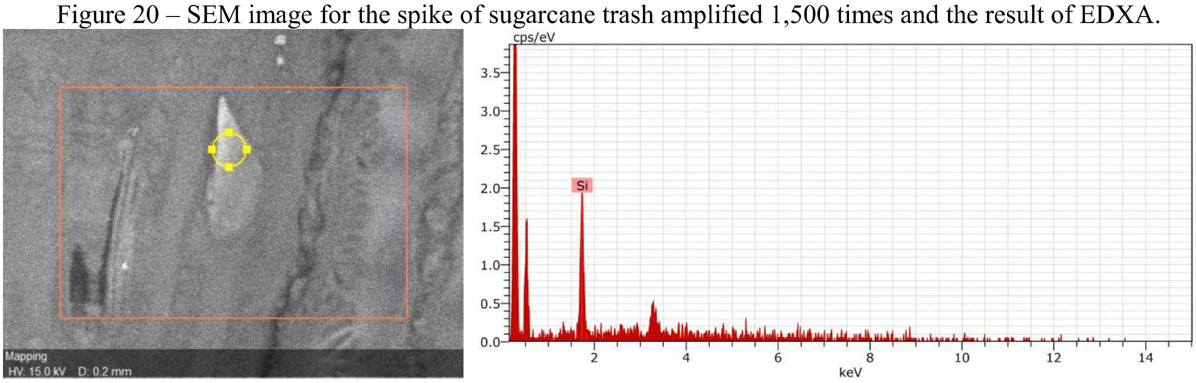
Source: author.

Figure 19 - SEM image of sugarcane leaf surface amplified 1,500 times.



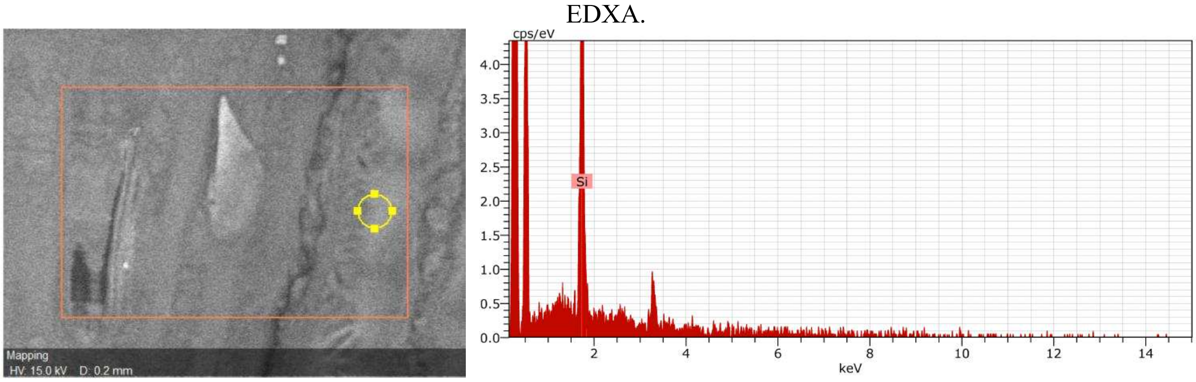
Source: author.

Figure 20 – SEM image for the spike of sugarcane trash amplified 1,500 times and the result of EDXA.



Source: author.

Figure 21 – SEM image for the structure of the sugarcane leaf surface amplified 1,500 times and the result of EDXA.



Source: author.

2.4. CONCLUSIONS

- The sample particle size affects the results. The samples particle size should be chosen carefully according to the test purpose.
- It is possible to outdoor storage (up to 2 years) for the sugarcane trash without changing the properties;
- The sugarcane trash recovering process affects the quality of the material by contamination from the soil;
- The contamination is concentrated in smaller particle size (<0.25mm);
- The variation in ash content (up to 2.61%) did not affect the HHV for sugarcane trash;
- The cleaning process in running water can reduce the contamination in sugarcane trash. In industrial scale it is difficult to use water due the environmental problems;
- The high amount of ash content in the sugarcane trash may cause abrasion and wear in the equipment.

CHAPTER 3 – CHEMICAL CHARACTERIZATION OF SUGARCANE TRASH STORED FOR BIOENERGY

3.1. INTRODUCTION

There are several factors to consider before qualifying a vegetable biomass to be used as a raw material for solid biofuel, regardless their availability in large amount. For example, the chemical composition of this residue (lignocellulosic materials), usually directly influence their energy performance, favoring or disfavoring its high heating value (HHV) and their behavior during combustion (MORAIS, 2007). Thus, it is known that high percentages of lignin, α-cellulose and fixed carbon are related to a higher calorific value and a slower combustion, raising the durability of the fuel burns.

In addition to the lignocellulosic nature, there are also extractives, chemical compounds in small quantities that are soluble in water and in organic solvents; among extractives there are terpenes, resins, volatile oils, fatty acids, waxes, tannins, and low molecular mass carbohydrates (JENKINS, 1990). The energy contribution for the HHV from the extractive depends on their chemical composition. And this ranges from plant sources and in accordance with the age and the tissue of the lignocellulosic material subjected to combustion (SANTOS et al., 2012).

The chemical composition of the biomass plays an important role for its energetic performance. Samuelsson et al. (2012) evaluated how, time storage and method of biomass storage can influence its chemical composition, overall regarding moisture and extractives content, and also in the compacted material durability, in different shapes of densified materials (pellets and briquettes).

It is important to know the physical and chemical properties of a material before using it as solid biofuel. The analysis of all the results provided by the characterization of the raw material allows evaluate it in order to address bottlenecks related to processing and quality of briquettes.

One of the challenges faced by sugar and alcohol sector is how to use the sugarcane trash. According to Leal et al. (2013), an average of 14 to 18% of sugarcane plant results in the trash, which corresponds to 10 to 18 $Mg.ha^{-1}$ of sugarcane trash available for energy purposes. The trash and the bagasse have different characteristics, although originated by the same plant. Bagasse is also a waste generated from sugarcane, it is already being used by the own power plants for boiler feed. The chemical and morphological peculiarity of sugarcane demand more research in this area (HOFSETZ and SILVA, 2012; MARABEZI, 2009).

The aim of the study was the chemical characterization of sugarcane trash in different storage time aimed the energy purpose.

3.2. MATERIAL AND METHODS

3.2.1. Material

The sugarcane trash used in this study was collected at ‘Fazenda Corredeira’, located in the municipality of Ibaté (21.9547°S, 47.9967°W) in São Paulo State. The farm has a planted area of 800 ha of sugarcane with an average yield of 87 tons. ha^{-1}. $year^{-1}$. The sugarcane varieties planted are RB 855453, RB 867515, RB 855536, SP 803280, SP 813250.

The samples were collected directly from the bales stored on the field (outdoor storage). Samples from the surface (outside) and the inner (inside) of different bales were collected. The purpose was to evaluate the surrounding (soil, rain, wind) effects on the bales and the variation of storage time the sugarcane straw. The storage time was 0, 1 and 2 years. The total treatments were: 0 year; 1 year inside; 1 year outside; 2 years inside and 2 years outside.

The straw sugarcane was oven dried, crushed using a vertical rotor mill with fixed and mobile knives Willey MA -340. Samples with 60 mesh (0.25mm) and 0% moisture content were used.

3.2.2. Extractives

The determination of extractives was carried out in 3 steps according to TAPPI standards T204-cm97 and T207-cm99 adapted. The first step was performed for extracting non-polar substances with the organic solvent cyclohexane 1:1 ethanol. In each soxhlet set, they were placed 3 packages with 2.0g each of sugarcane trash. For this extraction, the heaters were adjusted to promote boiling and maintained for about 24 cycles (5 hours). The packages were removed, taken to the oven at 105 ± 2°C until constant weight. For the second step it was used ethanol as a solvent in the soxhlet. The procedure was the same used in the first step. The third step was performed with hot water to remove polar components. The packages were placed in an Erlenmeyer flask with 1 L of deionized water and kept in a hot plate with constant stirring for 3 hours while maintaining the water level. The material was dried in an oven at 105±2°C until constant weight.

3.2.3. Klason Lignin Content

The insoluble Klason lignin content was determined according to standard TAPPI T222-om11. In a beaker with 1.0 g of free extractives material (0% moisture content) it was added 15.0 mL of H_2SO_4 72% (by temperature 10 to 15°C) in small portions. This mixture was kept in a water bath at 2°C for the dispersion material. After the dispersion, the system was covered with a watch glass and kept in a water bath at 20±2°C for 2 hours with frequent stirring. In a 1L Erlenmeyer flask were added 300 ml of water and then transferred the material in the beaker to the Erlenmeyer flask. The solution was diluted to H_2SO_4 3% and boiled for maintaining constant volume for 4 hours. After an overnight stay, the insoluble material decanted for filtration. The solution was filtered, washed with deionized water and placed in an oven at 105 ± 2°C until constant weight.

3.2.4. Holocellulose Content

The holocellulose content was determined based on TAPPI T9m-45. In an Erlenmeyer flask 500 mL was added 3.0 g of sugarcane trash (dry and extractive-free) and 120 mL of distilled water. The system was brought to a water bath at a constant temperature of 70°C. They were added 2.5 g of sodium chlorite ($NaClO_2$) and 1 mL of glacial acetic acid. The system was covered with the aid of a 50 mL beaker and kept in a water bath for one hour under constant stirring. Again, it was added 2.5 g of sodium chlorite and 1 mL of acetic acid, the reaction being maintained for another hour. After this time, it was added 2.5g of sodium chlorite and 1 mL of acetic acid and the reaction will continue for three hours. Subsequently, the system was cooled in an ice bath for about 30 minutes, and then the flask contents filtered in Büchner funnel. The material retained on the funnel was rinsed with distilled water and acetone until reaching neutral pH, subsequently brought in an oven at 105 ± 2°C for drying to constant weight.

3.2.5. High Heating Value (HHV)

The high heating value was adapted from ASTM D 5865-98, in duplicate, using 1.0 g samples of the material in a bomb calorimeter IKA C200 with isoperibol method.

3.2.6. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analyzer (EDXA)

The ashes of Klason lignin and holocellulose of the sugarcane trash were analyzed by scanning electron microscopy (SEM). Samples were placed on an aluminum base and fixed in a carbon tape. Prepared samples were kept in a desiccator until the time of analysis. To obtain the images it was used scanning electron microscopy Hitachi TM3000 operated with an acceleration voltage of 15kV with Energy Dispersive X-ray Analyzer (EDXA).

3.2.7. Statistical Analysis

Extractives, Klason lignin, holocellulose, HHV were statistically evaluated by Anova. The Tukey test was applied at 5% significance level for treatments that showed significant differences. All statistical analyzes were performed by R 2.11.1 software. (R STUDIO, 2012; R DEVELOPMENT CORE TEAM, 2008).

3.3. RESULTS AND DISCUSSION

3.3.1. Chemical Characterization

The Table 4 shows the chemical composition according to the sugarcane trash storage time.

Table 4 - Compositional analysis of sugarcane straw. The averages followed by the same letter do not differ statistically by Tukey test at 5% significance level.

	Storage time									
	0 year		1 year inside		1 year outside		2 years inside		2 years outside	
Extractives (%)	16.78±1.8	a	12.75±1.3	c	14.47±0.4	b	13.01±1.18	bc	13.99±0.29	bc
Klason Lignin (%)	34.83±2.26	a	33.40±4.97	a	35.95±4.20	a	35.21±6.39	a	38.76±3.77	a
Holocellulose (%)	65.93±7.17	a	66.50±0.14	a	66.75±0.75	a	66.43±1.76	a	67.92±1.67	a
Ash (%)	8.9		9.45		8.11		5.19		5.97	
Total	108.64		103.2		109.06		109.46		114.7	

*The averages followed by the same letter do not differ statistically by Tukey test at 5% significance level.

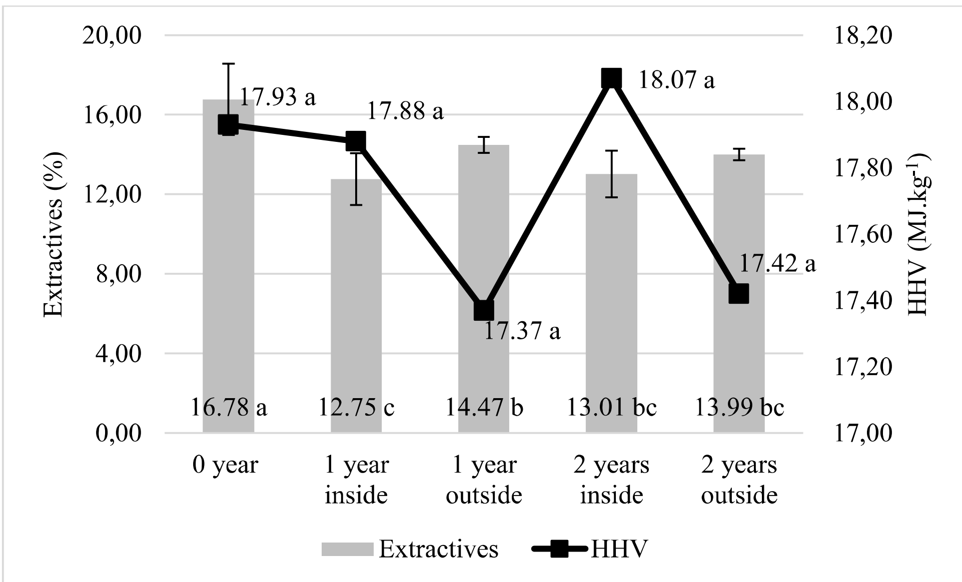
Szczerbowski et al. (2014) obtained 77.71% for holocellulose (hemicellulose + alpha cellulose) for sugarcane straw. Santos et al. (2014) found for holocellulose an average of 75%, for ash content 4.9%, and extractives 17%. The results for holocellulose content (Tab.4) showed lower results than Szczerbowski et al. (2014) and Santos et al. (2014). It was observed the presence of mineral contaminants in the filtered holocellulose. It was proven by the ash content. And the ash content presented high variation (from 5.19% to 9.45%) among the storage time treatments.

According to Mos et al. (2013), the senescence of the plant presents a degradation of cellular components and molecules such as proteins, lipids and carbohydrates. Therefore, it was expected that the higher storage time resulted in the lower percentage of carbohydrates in sugarcane straw. The table 4 did not show any statistical difference among the storage time treatments for holocellulose. It indicates that there was no degradation by storage time of the material.

The variations observed in the results of different authors may occur due to use of different materials and/or methods (SZCZERBOWSKI et al., 2014). The results for Klason lignin were considered high and can be explained due to the high amount of material impurities.

The Fig. 22 shows the results of HHV of the materials compared to the extractives content in all treatments.

Figure 22 - Extractives (%) x High Heating Value ($MJ.kg^{-1}$) for storage time treatments.

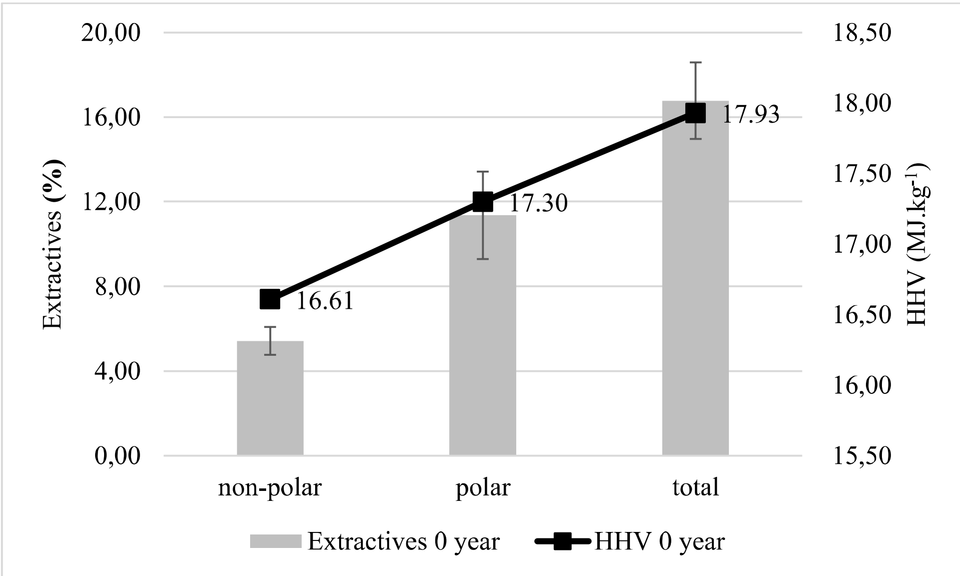


*The averages followed by the same letter do not differ statistically by Tukey test at 5% significance level.

Demirbas (2005) reported that materials with extractives-free had lower HHV. It showed the influence of the extractives in HHV. The results showed that the extractives content varied 4.03% (from 12.75% to 16.78%). The variation among HHV was 0.7 $MJ.kg^{-1}$ (from 17.37 to 18.07 $MJ.kg^{-1}$). The variation in HHV represented 4.0% and there was no statistical difference. It showed that the variation in 4.03% in extractives had no influence in HHV.

The Fig. 23 shows the results of HHV of the materials compared to the extractives (non-polar, polar and total).

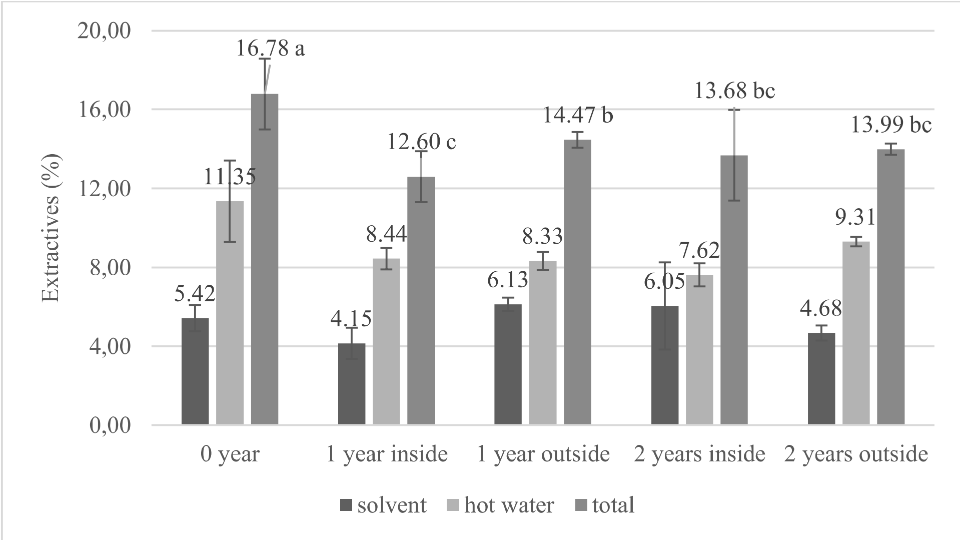
Figure 23 - Graphic showing the relation of 0 year extractives compounds (%) and High Heating Value ($MJ.kg^{-1}$) of sugarcane trash.



The Fig. 23 shows the material (treatment 0 year) presented 17.93 $MJ.kg^{-1}$. Without polar extractives the HHV was 17.30 $MJ.kg^{-1}$. And without non-polar extractives the HHV was 16.61 $MJ.kg^{-1}$. It was expected that without non-polar it would result in lower HHV due the extraction of waxes and oils (components with high calorific value). Szczerbowski et al. (2014) found that sugarcane trash has many components that can be extracted into water. The hot water soluble extractives presented less caloric value compared to waxes and oils. It was expected that without this polar content, the higher HHV than HHV without non-polar. The best result for HHV was the treatment with polar and non-polar constituents (total). The extractives contribute to increase the HHV.

The Fig. 24 shows the results of extractives content of sugarcane trash of different solvents.

Figure 24 - Extractives content of sugarcane trash of different solvents.

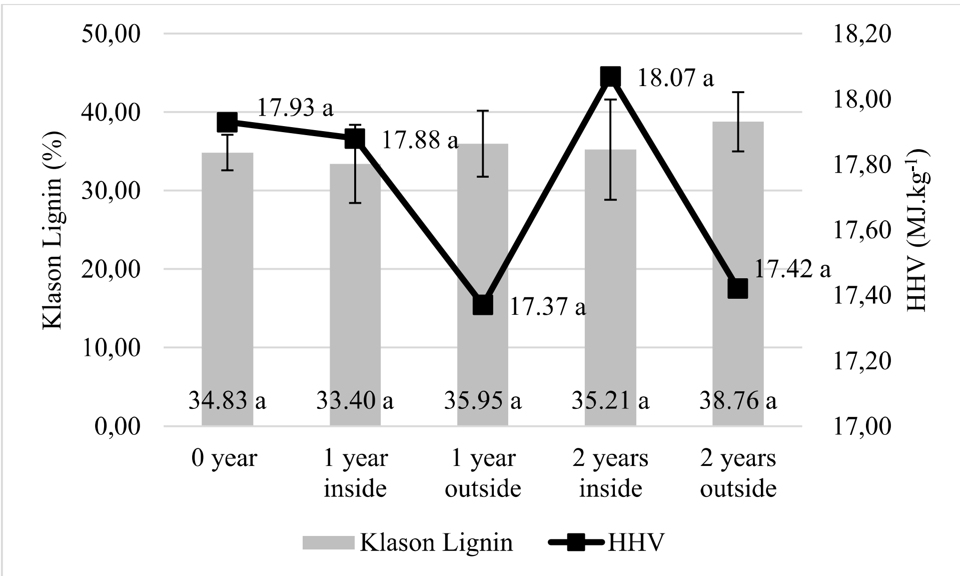


*The averages followed by the same letter do not differ statistically by Tukey test at 5% significance level.

The extractives showed a reduction for the 0 year treatment to 2 years treatment (Fig. 24). It was noticed that the reduction had more impact on extractives in hot water (polar), which shows the influence of leaching in bales. Mos et al. (2013) assign a decrease in the amount of ash by rain washing the bale surface, when they are stored on the field.

The results for Klason lignin and HHV are shown in Fig. 25.

Figure 25 - Klason Lignin (%) x High Heating Value (MJ. kg^{-1}) for storage time treatments.



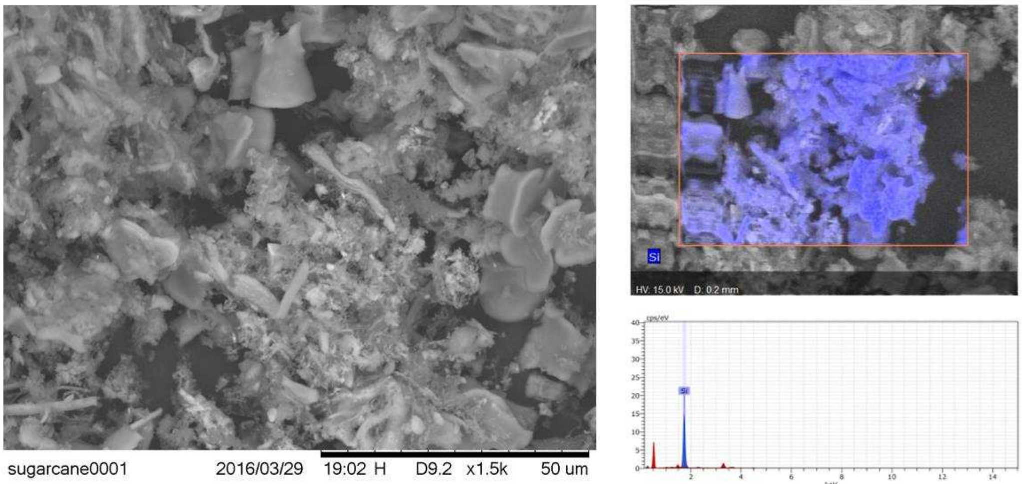
*The averages followed by the same letter do not differ statistically by Tukey test at 5% significance level.

The results of lignin content ranged from 33 to 39% (Fig. 25). Landell et al. (2013), Oliveira et al. (2013) and Szczerbowski et al. (2014) obtained as results for sugarcane straw, 25.96%, 22.5% and 20.57%, respectively. All the averages were higher compared to the average found in the literature. According to Liu et al. (2010) and Fernandes et al. (2009), cellulose, hemicellulose and lignin may vary with the plant tissue, age, storage, collection and location. According to Greenhalf et al. (2013) the increase in lignin can increase the heating value of the biomass material in combustion. The results for Klason lignin and HHV shown in Fig. 27 showed little variation and did not differ statistically.

3.3.2. Scanning Electron Microscopy (SEM) and Energy Dispervisive X-ray Analyzer (EDXA)

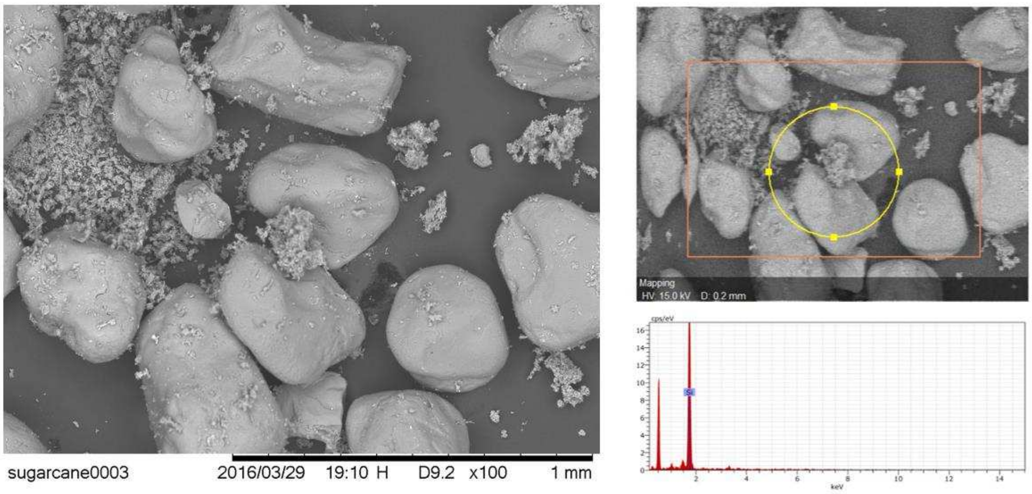
The SEM-EDXA was used to help to identify the ashes of Klason lignin and holocellulose. The images justify the high results obtained, mainly for lignin. Fig. 26-31 show the images of SEM and the results of analysis by EDXA. All the images present silica, sometimes as inorganic element from the sugarcane leaf itself (Fig. 26) and other shaped in stones such as mineral impurities (Fig. 27, 29, 31).

Figure 26 – SEM image and EDXA from ash from Klason lignin content.



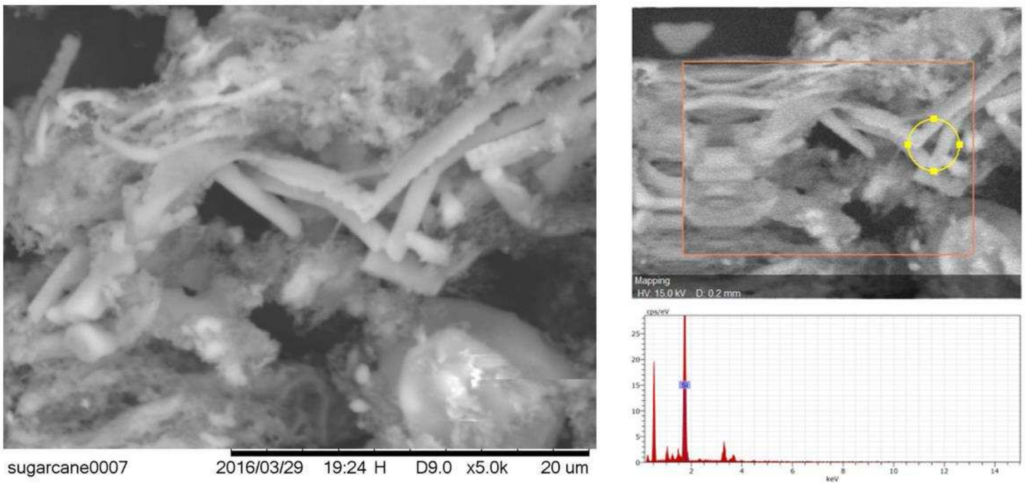
Source: author.

Figure 27 - SEM image and EDXA from ash from Klason lignin content.



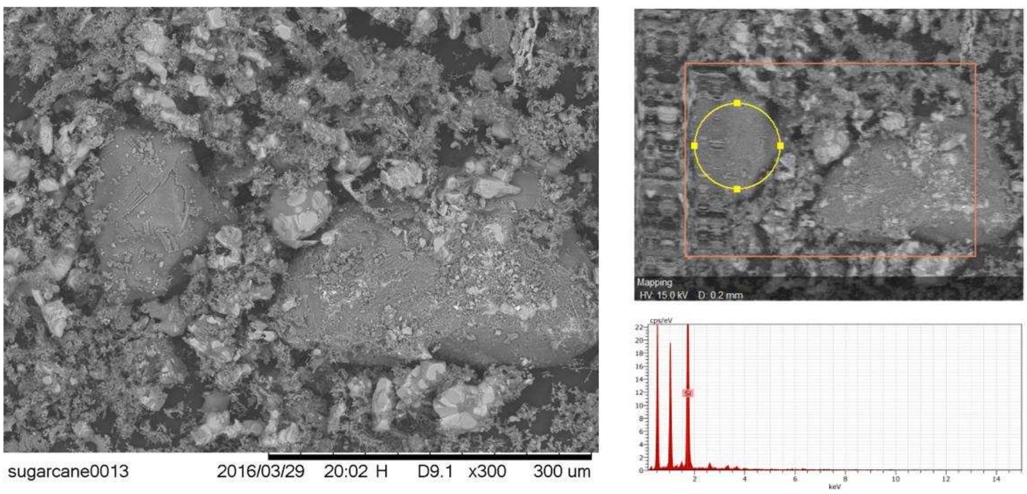
Source: author.

Figure 28 - SEM image and EDXA from ash from Klason lignin content.



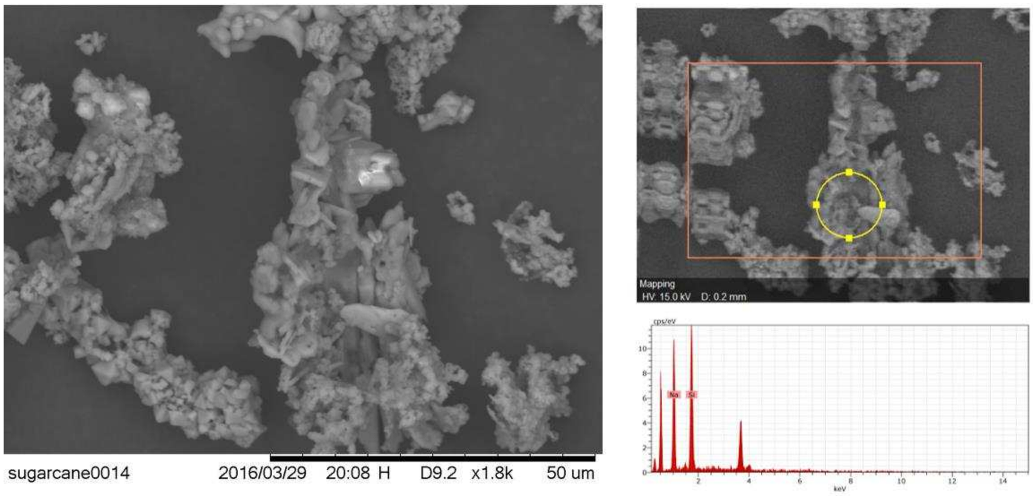
Source: author.

Figure 29 - SEM image and EDXA from the ashes from Holocellulose content.



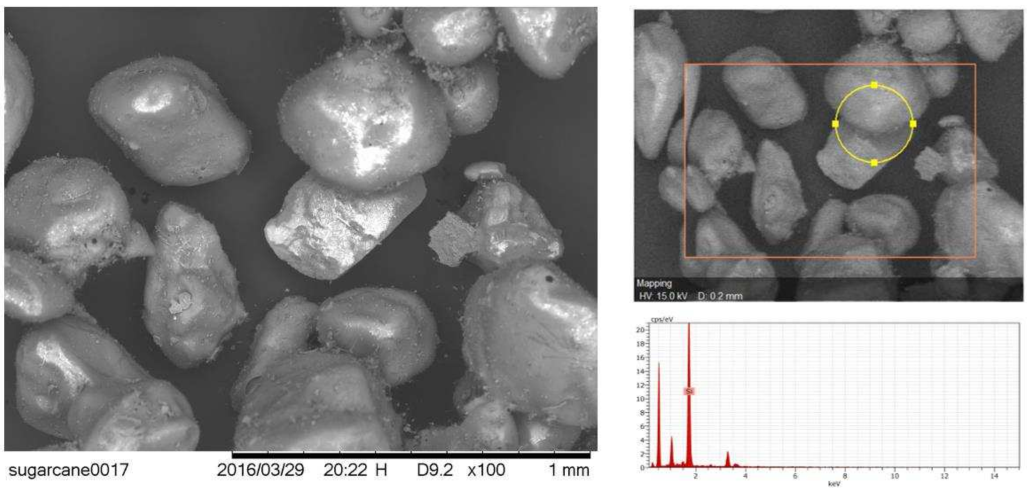
Source: author.

Figure 30 - SEM image and EDXA from the ashes from Holocellulose content.



Source: author.

Figure 31 - SEM image and EDXA from the ashes from Holocellulose content.



Source: author.

3.4. CONCLUSION

- The storage time did not affect the content of holocellulose and Klason lignin;
- The extractives can be affect (decrease) by the storage time;
- The high amounts of mineral impurities (ashes) affected (raised) the results for Klason lignin;
- A difference of 27% in ash content did not affect HHV;
- The storage time did not affect the characteristics of the material for energy purpose.

CHAPTER 4 – GENERAL CONCLUSION

4.1. GENERAL CONCLUSION

The sugarcane trash has great potential for energy purposes. The cultivation of sugarcane in Brazil occupies about 9 million ha, representing 1.06 % of the territory. The 2015/2016 sugarcane crop is estimated at 590 million tons.

In Brazil, some laws were created to eliminate the use of fire in sugarcane plantations. The trash and bagasse represent two thirds of the sugarcane biomass. It is estimated an average generation of 14 $ton.ha^{-1}$ of trash on a dry basis. Due to the favorable conditions of the trash coverage there is an increase of pests which can cause damage to the plantation. Even contributing to the maintenance of nutrients and soil conservation, the trash recovering can lead to problems, raising the management costs of culture. In order to avoid pesticide cost and others problems in remain the sugarcane trash on the fields, it is necessary to remove it. A solution would be the mechanized collection of trash, which could be used for energy purposes. This material has great potential to improve and diversify the Brazilian energy matrix.

The problem for the use of this biomass in mechanical harvesting is how to recover and make it available in the most appropriate way. To recover the material in bales is necessary to raking the trash scattered on the ground.

It is necessary to improve the process of recovery and cleaning of sugarcane trash. The cleaning machines used for this process are not sufficient to remove the impurities from the soil. The major problems are the impurities adhered to the trash, raising its ash content. The ash content is a characteristic that is undesirable for the biomass. The ashes can lead to wear the equipment, cause corrosion and increased amount of maintenance in the boiler.

The greater concentration of ash content was found for the fraction of fine particles (<60 mesh), representing twice the ash content of coarser particles. It was expected that higher ash content will result in lower HHV. The fraction <60mesh presented higher ash content (6.5% to 12.7%) but there was no significant difference in HHV, which may have been driven by the percentage of extractives content in the material. According to Bridgeman et al. (2011) the larger particles fractions hold greater amount of cellulose, hemicellulose and lignin and in smaller fractions there is a concentration of soluble small molecules (extractives).

In general, it can be concluded with this work that the particle size influences the biomass quality. The particle separation allows the removal of the finer particles, which has the highest ash content. The impurities are concentrated in smaller particles and interfere in chemical characterization (holocellulose and lignin content). The storage time did not affect the characteristics of the material for energy purpose.

The manufacturer of briquettes production line was responsible for solving the problem of abrasion in briquetting machine. Until the conclusion of this work, the manufacturer had not provided answers to the resolution of the equipment wear.

4.2. REFERENCES

ANDRIETTA, M.G.S.; STECKELBERG, C.; ANDRIETTA, S.R. Bioetanol – Brasil, 30 anos de vanguarda. **Multiciência: Construindo a história dos produtos naturais**, Campinas, n.7, 2006. Disponível em: < https://www.multiciencia.unicamp.br/artigos_07/a_02_7.pdf>, acesso em: 01/09/2015

AMERICAN SOCIETY FOR TESTING AND MATERIALS. **D1102-84**: standard test method for ash in wood. Phyladelphia, 2007. 2 p.

_____. **D5865-98**: standard test method for gross calorific value of coal and coke. Phyladelphia, 1998. 10 p.

_____. **E872-82**: standard test method for volatile matter in the analysis of particulate wood fuels. Phyladelphia, 2006. 3p.

BAXTER, L.L. et al.; The behavior of inorganic material in biomass-fired power boilers: field and laboratory experiences. **Fuel Processing Technology**, v. 54, p. 47-78, 1998.

BHATTACHARYA, S. C.; SETT, S.; SHRESTHA, R. M State of the art for biomass densification. Energy Sources. New York. v. 11, n. 3, p. 161-182, 1989.

BRAND, M. A. **Energia de biomassa florestal**. Rio de Janeiro: Interciência, 2010. 114p.

BRAND, M.A.; MUÑIZ, G.I.B. Influência da Época de Colheita e da Estocagem na Composição Química da Biomassa Florestal. **Floresta e Meio Ambiente**, v. 19, n.1, p. 66-78, 2012.

BRASIL. Decreto lei n.: 2.661, 08 de jul. de 1998. **Diário Oficial da República Federativa do Brasil.** Seção 1. Edição 129 de 9 jul. de 1998. p. 25. Disponível em http://pesquisa.in.gov.br/imprensa/jsp/visualiza/index.jsp?jornal=1&pagina=25&data=09/07/1998

BRASIL, D.S.; MARTINS, M.P.; NAKASHIMA, G.T.; YAMAJI, F.M. Use of sugarcane bagasse and candeia waste for solid biofuels production. **Floresta**, Curitiba, v.45, n.1, p.185-192, 2015. DOI:10.5380/rf.v45i1.36502

BRAUNBECK, O. A.; BIANCHI, A. D. Carregamento mecânico – redução de impurezas minerais. **Boletim Técnico Copersucar**, n. 43, p. 35-42, jul.1988.

BRIDGEMAN, T.G. et al. Influence of particle size on the analytical and chemical properties of two energy crops. **Fuel**, 86, p.60-72, 2007.

CERQUEIRA-LEITE, R. C. Estudo sobre as possibilidades e impactos da produção de grandes quantidades de etanol visando à substituição parcial de gasolina no mundo. Fase 2. **Relatório Final. Projeto CGEE-Nipe**, Unicamp, 2007.

CONAB - Companhia Nacional de Abastecimento. Perfil do Setor do Açúcar e do Álcool no Brasil - Edição para a safra 2008-2009. Brasília, 80 p., 2010.

_____. Acompanhamento da safra brasileira de cana-de-açúcar. Safra 2014/2015. v.1. n.3 – terceiro levantamento. Brasília, p. 1-27, dez. 2014.

DEMIRBAS, A. Recent advances in biomass conversion technologies. **Energy Edu Sci Technology**, 6, p. 19-40, 2000.

_____. Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues. **Progress in energy and combustion in science**, 31, p.171-192, 2005.

DIAS, M.O.S. et al. Second generation ethanol in Brazil: Can it compete with electricity production? **Bioresource Technology**, v.102, n.19, p. 8964-8971, 2011.

DINARDO-MIRANDA, L. L.; COELHO, A. L.; FERREIRA, J. M.G. Influência da época de aplicação de inseticidas no controle de Mahanarva fimbriolata (Stål) (Hemiptera: Cercopidae), na qualidade e na produtividade da cana-de-açúcar. **Neotrop. Entomol.**, Londrina, v. 33, n. 1, p. 91-98, 2004.

EMPRESA DE PESQUISA ENERGÉTICA. Balanço Energético Nacional 2015 – Ano base 2014: Relatório Síntese. 62 p. Rio de Janeiro: EPE, 2015.

FERNANDES, T.V. et al. Effects of themo-chemical pre-treatment on anaerobic biodegradability and hydrolysis of lignocellulosic biomass. **Bioresource Technology**, 100, p. 2575-2579, 2009.

FRANCO, F. N. **Alguns parâmetros de desempenho operacional de um sistema de recolhimento de palhiço de cana-de-açúcar (Saccharum spp.) a granel.** 2003. 113 p. Dissertação (Mestrado) – Escola Superior de Agricultura "Luiz de Queiroz", Universidade de São Paulo, Piracicaba, 2003.

GARCÍA, R. et al. Biomass proximate analysis using thermogravimetry. **Bioresource Technology**, 139, p.1-4, 2013.

GOLDEMBERG, J.; COELHO, S.T.; GUARDABASSI, P. The sustainability of ethanol from sugarcane. **Energy Policy**, 36, p. 2086 – 2097, 2008.

GÓMEZ, E.O. et al. Sugarcane trash as feedstock for second generation processes. In: CORTEZ, L.A.B. **Sugarcane Bioethanol: R&D for productivity and sustainability**, São Paulo: Edgar Blucher, 2010. p.637-659.

GONÇALVES, B.F. et al. Caracterização e comparação entre diferentes granulometrias de serragem de Eucalyptus grandis para a confecção de briquetes. **Rev. Inst. Flor.**, v.25, n.2, p.205-213, 2013.

GREENHALF, C.E. et al. The influence of harvest and storage on the properties of fast pyrolysis from Miscanthus x giganteus. **Biomass and Bioenergy**, 56, p. 247-259, 2013.

HASSUANI, S. J.; LEAL, M.R.L.V.; MACEDO, I.C. Biomass power generation: sugarcane bagasse and trash. In: **Série Caminhos para Sustentabilidade**. Piracicaba: PNUD-CTC; 2005.

HOFSETZ, K.; SILVA, M.A. Brazilian sugarcane bagasse: Energy and non-energy consumption. **Biomass and Bioenergy**, 46, p.564-573, 2012.

IBÁ. Relatório Ibá 2015. Brasília: 2015. 64 p. Disponível em: <http://iba.org/images/shared/iba_2015.pdf>.Acesso em: 18 abr. 2016

JENKINS, B.M. et al. Combustion properties biomass. **Fuel Processing Technology**, 54, p. 17-46, 1998.

JENKINS, B. M. Fuel Properties for Biomass Materials. **International Symposium on Application and Management of Energy in Agriculture: The Role of Biomass Fuels**. Delhi, India, p. 21-23, 1990.

KORNDÖRFER, G.H.; LEPSCH, I. Chapter 7 Effect of silicon on plant growth and crop yield. **Studies in Plant Science**, v. 8, p. 133-147, 2001.

LANDELL, M.G.A. et al. Residual biomass potential of commercial and pre-commercial sugarcane cultivars. **Sci. agric.**, Piracicaba [online]. 2013, vol.70, n.5, pp. 299-304. ISSN 0103-9016.

LEAL, M.R.L.V. et al. Sugarcane straw availability, quality, recovery and energy use: A literature review. **Biomassa and Bioenergy**, 53, p. 11-19, 2013.

LEHTIKANGAS, P. Quality properties of pelletised sawdust, logging residues and bark. **Biomass and Bioenergy**, v.20, p. 351-360, 2001.

LENÇO, P. C. **Caracterização do bagaço de cana-de-açúcar para geração de energia.** 2010. 181f. Tese. Universidade Estadual de Campinas, Campinas, 2010.

LIU, L. et al. Variability of biomass chemical composition and rapid analysis using FT-NIR techniques. **Carbohydrates Polymers**, 81, p.820-829, 2010.

LOGANATHAN, P. **Soil quality considerations in the selection of sites for aquaculture**. Food and Agriculture Organization of the United Nations, 1987. Disponível em: < http://www.fao.org/docrep/field/003/ac172e/AC172E03.htm>. Acesso em: 15 abr. 2016.

LU, G.Q. et al. Fundamental study on combustion characteristics of biobriquette. **Kagaku Kogaku Ronbun**, n. 23, p.23-31, 1997.

MADALENO, L.L. et al. Influence of Mahanarva fimbriolata (Stål) (Hemiptera: Cercopidae) injury on the quality of cane juice. **Neotropical Entomology**, v. 37, n.1, p. 68-73, 2008.

MARABEZI, K. **Estudo sistemático das reações envolvidas na determinação dos teores de lignina e holocelulose em amostras de bagaço e palha de cana-de-açúcar.** 2009. 158f. Dissertação. Universidade de São Paulo, São Carlos, 2009.

MARTELLI, R.; BENTINI, M.; MONTI, A. Harvest storage and handling of round and square bales of giant reed and switchgrass: An economic and technical evaluation, **Biomass and Bioenergy**, Volume 83, December 2015, Pages 551-558,

MEYER, D. et al. Brazilian Ethanol: Unpacking a Success Story of Energy Technology Innovation. **Historical Case Studies of Energy Technology Innovation**. In: Chapter 24, **The Global Energy Assessment**. GRUBLER, A. et al. Cambridge University Press: Cambridge, UK, 2012

MICHELAZZO, M.B.; BRAUNBECK, O.A. Análise de seis sistemas de recolhimento do palhiço na colheita mecânica da cana-de-açúcar. **R. Bras. Eng. Agríc. Ambiental**, v.12, n.5, p.546–552, 2008.

MORAIS, D. M. **Briquetes de resíduos ligno-celulósicos como potencial energético para a queima de blocos cerâmicos: aplicação em uma indústria de cerâmica vermelha que abastece o Distrito Federal**. 2007. 265f. Tese (Doutorado em Estruturas e Construção Civil), Departamento de Engenharia Civil e Ambiental. Universidade de Brasília, Brasília, 2007.

MOS, M. et al. Impact of Miscanthus x giganteus senescense times on fast pyrolysis bio-oil quality. **Bioresource Technology**, v.129, p.335-342, 2013.

MUNDIM, D.A.; PELISSARI, H.N.T.; PEREIRA, F.J.S. Panorama da colheita mecanizada de cana-de-açúcar e seu impacto no manejo da cultura. **Nucleus**, edição especial, 2009.

NAIK, S. et al. Characyerization of Canadian biomass for alternative renewable biofuel. Renewable Energy, v. 35, p. 1624-1631, 2010.

NAKASHIMA, G.T.; MARTINS, M.P.; SILVA, D.A.; CHRISOSTOMO, W.; YAMAJI, F.M. Aproveitamento de resíduos vegetais para a produção de briquetes. **Revista Brasileira de Ciências Ambientais**, n. 34, p. 22-29, 2014.

OLIVEIRA, F.M.V. et al. Industrial-scale steam explosion pretreatment of sugarcane straw for enzymatic hydrolysis of cellulose for production of second generation ethanol and value-added products. **Bioresource Technology**, v.130, p.168-173, 2013

PAULÍNIA (município). Lei n° 1952 de 20 de dezembro de 1995. Disponível em:< https://leismunicipais.com.br/a/sp/p/paulinia/lei-ordinaria/1995/196/1952/lei-ordinaria-n-1952-1995-dispoe-sobre-a-proibicao-de-queimadas-no-municipio-de-paulinia-nas-formas-que-especifica-e-da-outras-providencias?q=1952->. Acesso em: 15 abr. 2016

PELÁEZ SAMANIEGO, M. R. **Uso de biocombustível da pirólise rápida da palha de cana em um motor de ciclo Otto**. 2007. 100 p. Dissertação – Faculdade de Engenharia Mecânica, FEM, Unicamp, Campinas, 2007. Disponível em: < http://www.bibliotecadigital.unicamp.br/document/?code=vtls000421869&fd=y>. Acesso em: 18 abr. 2016

PETTERSEN, R. C. The chemical composition of wood. In: ROWELL, R.M., ed. **The chemistry of solid wood. Advances in chemistry**, vol. 207. Washington: American Chemical Society, ISBN 0-8412-0796-8; 1984: Chapter 2.

PROTÁSSIO, T.P. et al. Relação entre o poder calorífico superior e os componentes elementares e minerais da biomassa vegetal. **Pesquisa Florestal Brasileira**, v. 31, n.66, p. 113-122, 2011.

RAVEENDRAN, K.; GANESH, A. A flash pyrolysis of sunflower oil cake for production of liquid fuels. **Fuel**, v. 75, p. 1715-1720, 1996.

R DEVELOPMENT CORE TEAM. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria, 2008. ISBN 3-90005107-0

R STUDIO. RStudio: Integrated development environment for R (Version 0.96.122) [Computer software]. Boston, MA, 2012.

RAVANELI, G.C. et al. Danos promovidos pela cigarrinha-das-raízes sobre a qualidade tecnológica da cana. **Ciência & Tecnologia: FATEC-JB**, Jaboticabal, v. 3, n. 1, p. 16-27, 2011. ISSN 2178-9436.

RHÉN, C. et al. Effects of raw material moisture content, densification pressure and temperature on some properties of Norway spruce pellets. **Fuel Processing Technology**, v. 87, p. 11-16, 2005.

RIBEIRO, H.; ASSUNÇÃO, J.V. Efeitos das queimadas na saúde humana. **Estudos avançados USP**, São Paulo, n. 44, p.125-148, 2002.

RIBEIRO, H.; FICARELLI, T.R.A. Queimadas nos canaviais e perspectivas dos cortadores de cana-de-açúcar em Macatuba, São Paulo. **Saúde Soc. São Paulo**, v.19, n.1, p.48-63, 2010.

RÍPOLI, T.C.C.; MOLINA JR, W.F.; RÍPOLI, M.L.C. Energy potential of sugar cane biomass in Brazil. **Scientia Agricola**, v.57, n.4, p.677-681, 2000.

RÍPOLI, T.C.C.; RÍPOLI, M.L.C. Biomassa de cana-de-açúcar: Colheita, energia e ambiente. Piracicaba: edição dos autores, 2004. 302 p.

RÍO, J.C. et al. Differences in the chemical structure of the lignins from sugarcane bagasse and straw. **Biomass and Bioenergy**, v. 81, p. 322-338, 2015.

SAMUELSSON, R.; LARSSON, S. H.; THYREL, M.; LESTANDER, T. A. Moisture content and storage time influence the binding mechanisms in biofuel wood pellets. **Applied Energy**, v. 99, p. 109-115, 2012.

SANDERSON, M. A.; EGG, R. P.; WISELOGEL, A. E. Biomass losses during harvest and storage of switchgrass, **Biomass and Bioenergy**, Volume 12, Issue 2, 1997, Pages 107-114.

SANTOS, I. D**. Influência dos teores de lignina, holocelulose e extrativos na densidade básica e contração da madeira e nos rendimentos e densidade do carvão vegetal de cinco espécies lenhosas do cerrado.** 2008. 57p. (Dissertação Mestrado) – Universidade de Brasília, Distrito Federal, 2008.

SANTOS, F.A. et al. Potencial da palha de cana-de-açúcar para produção de etanol. **Quím. Nova**, São Paulo, v. 35, n. 5, p. 1004-1010, 2012.

SANTOS, F.A. et al. Otimização do pré-tratamento hidrotérmico da palha de cana-de-açúcar visando à produção de etanol celulósico. **Quím. Nova**, São Paulo, v. 37, n. 1, p. 56-62, 2014.

SÃO PAULO (Estado). Lei nº 11.241, de 19 de setembro de 2002. **Diário Oficial do Estado**, Poder Executivo, São Paulo, 20 set. 2002. Seção I, 112 (180). Disponível em: <https://www.imprensaoficial.com.br/Certificacao/GatewayCertificaPDF.aspx?notarizacaoID=7ffaae27-e636-41f2-847d-93eb87bf799a>. Acesso em: 7 abr. 2016.

_____. TRIBUNAL DE JUSTIÇA. Acórdão de 10 dez. 2007. **Site do Tribunal de Justiça de São Paulo**. Disponível em: < https://esaj.tjsp.jus.br/cjsg/getArquivo.do?cdAcordao=2395997>. Acesso em: 15 abr. 2016

SEABRA, J.E.A. et al. A techno-economic evaluation of the effects of centralized cellulosic ethanol and co-products refinery options with sugarcane mill clustering. **Biomass and Bioenergy**, v.34, n. 8, p. 1065-1078, 2010.

SEGGIANI, M. Empirical correlations of the ash fusion temperatures and temperature of critical viscosity for coal and biomass ashes. **Fuel**, v. 78, n.9, p. 1121-1125, 1999.

SILVA, D.A.; NAKASHIMA, G.T.; BARROS, J.L.; DA RÓZ, A. L.; YAMAJI, F.M. Caracterização de biomassas para a briquetagem. **Floresta**, Curitiba, v.45, n.4, p.713-722, 2015.

SOCCOL, C.R. et al. Bioethanol from lignocelluloses: Status and perspectives in Brazil. **Bioresources Technology**, 101, p. 4820-4825, 2010.

SOUZA, Z.M. et al. Sistemas de colheita e manejo da palhada de cana-de-açúcar. **Pesq. agropec. bras.**, Brasília, v.40, n.3, p.271-278, 2005.

SUPREMO TRIBUNAL FEDERAL. **Manifestação**. Disponível em: < http://www.stf.jus.br/portal/jurisprudenciarepercussao/verPronunciamento.asp?pronunciamento=2806387>. Acesso em: 22 set. 2015.

SZCZERBOWSKI, D. et al. Sugarcane biomass for the biorefinaries: Comparative composition of carbohydrate and non-carbohydrate components of bagasse and straw. **Carbohydrate Polymers**, 114, p.95-101, 2014.

TAMAKI, Y.; MAZZA, G. Measurement of structural carbohydrates, lignins, and micro-components of straw and shives: Effects of extractives, particle size and crop species. **Industrial Crops and Products**, v.31, p.534-541, 2010.

TECHNICAL ASSOCIATION OF PULP AND PAPER INDUSTRY. Standard Method **T203 cm-99** – Tappi Test Methods, 1999.

_____. **T204 cm-97** – Tappi Test Methods, 1997.

_____. **T207 cm-99** – Tappi Test Methods, 1999.

_____. **T211 om-02 –** Tappi Test Methods, 2002.

_____. **T222 om-02** – Tappi Test Methods, 2002.

_____. **T9m-45** – Tappi Test Methods, 1950.

TEIXEIRA, W.S. Cana-de-açúcar. In: CONAB - Companhia Nacional de Abastecimento. **Perspectivas para a agropecuária.** Brasília, v.2, p.55-62, set.2014.

TELMO, C.; LOUSADA, J. The explained variation by lignina and extractive contentes on higher heating value of wood. **Biomass and Bioenergy**, v. 35, p. 1663-1667, 2011.

TOWNSEND, W.N. **An Introduction to the Scientific Study of the Soil.**
Edward Arnold (Publishers) Ltd. U.K, 209pp, 1982.

TRIPATHI, A.K.; IYER, P.V.R.; KANDPAL, T.C. A techno-economic evaluation of biomass briquetting in India. **Biomass and Bioenergy**, v.14, n.5-6, p.479-488, 1998.

UNIÃO DAS INDÚSTRIAS CANAVIEIRAS. Açúcar e álcool do Brasil: Commodities da energia e do meio ambiente. São Paulo, 2004. Disponível em: <http://www.fat.uerj.br/intranet/disciplinas/Processos%20Organicos%20II/Acucar%20e%20alcool/Acucar%20e%20alcool%20do%20Brasil.pdf>, acesso em: 04 jun. 2015.

_____. Safra 2015/2016 no Centro-Sul deve atingir 590 milhões de toneladas de cana processadas, com prioridade para a produção de etanol. Disponível em: < http://www.unica.com.br/noticia/>. Acesso em: 24 set. 2015.

VASCONCELOS, G. C.; VERÍSSIMO, L. A. C.; SILVEIRA, A. A.; BIANCHINI, S. Energia lignocelulósica da biomassa: uma perspectiva sustentável. II Congresso Brasileiro de Agroecologia. **Rev. Bras. Agroecologia**, v. 2, n. 1, fev. 2007.

VASSILEV, S.V. et al. An overview of the chemical composition of biomass. **Fuel**, v. 89, p. 913-933, 2010.

YAMAJI, F.M. et al. ANÁLISE DO COMPORTAMENTO HIGROSCÓPICO DE BRIQUETES. **Energia na Agricultura**, Botucatu, v. 28, n.1, p.11-15, 2013.

YAMAN, S. Pyrolysis of biomass to produce fuels and chemical feedstocks. **Energy Conversion & Management**, v. 45, n. 5, p. 651-671, 2004.

YIN, C. Prediction of higher heating values of biomass from proximate and ultimate analysis. **Fuel**, v.90, p.1128-1132, 2011.