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EVALUATION OF THE INFLUENCE OF LIGNIN ON THE BIOMASS TORREFACTION PROCESS

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Abstract. *In the current scenario of the depletion of fossil fuel reserves, lignocellulosic biomass presents itself as an important source of energy because it is cheap and widely available. Researchers have been looking for ways to improve the thermo-chemical conversion processes of biomass to biofuels, in order to obtain an increase in the energy productivity of the same. A pretreatment that is being used for this purpose is torrefaction, in which the sample is submitted to temperatures between 200 °C and 300 °C under inert atmosphere, generating a product with high energetic density. In the chemical treatment known as acetosolv pulping, the delignification of the biomass occurs, generating black liquor rich in lignin and being insoluble in water, it is possible to recover the final of the process. This study aimed to verify the influence of lignin on the sugarcane bagasse torrefaction process, treating the biomass by the acetosolv pulp and isolating the lignin, aiming the energy optimization of the process. Based on analysis of the experimental results, it was observed that the lignin present in the biomass contributes significantly to its energy density because it provides better higher heating value and volatile ignitability values in the biomass.*

Keywords: *Torrefaction, Acetosolv, Biomass, Sugarcane Bagasse.*

1. INTRODUCTION

Currently, biomass represents a promising source of raw material for the generation of energy, presenting advantages such as low emission of polluting gases, cheap and easy to obtain, and acquired from energy crops and agricultural, forest and domestic waste (Ozturk et al., 2017). The annual production of this material is about 181.5 billion tons, presenting itself as a widely available resource (Paul and Dutta, 2018).

Biomass is capable of generating electricity, thermal energy and biofuels from conversion processes just as combustion, gasification and pyrolysis (Cai et al., 2018). Biomass in its natural state is considered a low quality raw material to be used directly in conversion processes since it has disadvantages, for example, high moisture content, low energy density and low grinding (Su et al., 2018).

The torrefaction has been extensively used as a pretreatment for the conversion processes, in which the sample is submitted to a temperature between 200 and 300 °C under inert atmosphere, resulting in improvements in its physical-chemical properties for further processing. In this method, cellulose, hemicellulose and lignin decompose during torrefaction, with reactions such as dehydration, decarbonization and deoxygenation, generating a hydrophobic product, being intermediate between biomass and coal, with high energy density and with better grinding performance (Macedo et al., 2014; Su et al., 2018; Zhang et al., 2018; Chen et al., 2018).

Thermogravimetric analysis (TGA) is commonly used to study the thermal behavior of fuels, and it is possible to verify important properties that directly influence the conversion processes like to ignition temperature and burnout, as well as data such as percentage of volatile material, fixed carbon, humidity and ash present in the sample (Ma et al., 2017; Li et al., 2019). Ignition temperature is the lowest temperature at which fuel ignites in the air without an external source, while burnout temperature is the temperature at which the sample is fully consumed (Guo et al., 2019).

Favored by geographic and natural conditions, Brazil has a large variety of renewable energy, able to produce biomass without competing with local agriculture (Borges et al., 2016). According to the most recent data published by the FAO (Food and Agriculture Organization of the United Nations) in 2017, Brazil was the largest producer of sugarcane, with production around 758 million tons (FAO, 2019). Sugarcane bagasse is obtained as a lignocellulosic residue after the sugar cane milling process in sugar-alcohol power plants and contains about 18 to 27 % of lignin in its composition (Pinheiro et al., 2017).

Lignin is the second most abundant organic substance in the cell wall of plants after cellulose, consisting of a highly complex amorphous polymer composed of 3 units of the phenylpropane monomer: p-coumarilic alcohol, coniferyl alcohol, and synapyl alcohol (Jönsson and Martín, 2016; Nogueira et al., 2019).

Among the methods of lignin extraction, the organosolv process stands out for obtaining a high quality lignin with low amount of associated ash and carbohydrates (Figueiredo et al., 2018; Nogueira et al., 2019). In this treatment, there is a mixture of organic solvents, such as acetic acid, with an inorganic acid, like hydrochloric acid, which act as a catalyst and promote the breakdown of the cell wall at high temperature, solubilizing part of the hemicellulose and lignin. The lignin is recovered at the end of the process by concentrating the solvent and precipitating it with water (Behera et al., 2014; Figueiredo et al., 2018; Nogueira et al., 2019).

The properties of the three main biomass components influence the torrefaction process. However, in the last 15 years, few studies have been done evaluating the influence on the yield of its products and by-products (Macedo et al., 2014; Chen et al., 2018).

The objective of this study was to evaluate the influence of lignin on the torrefaction process. For that, firstly, it was applied a delignification of the sugarcane bagasse by the organosolv pulping process, then, the lignin was isolated. All samples obtained were chemically and physically characterized, aiming at the energy optimization of the process.

2. MATERIALS AND METHODS

The study was performed in three stages: 1) Preparation of biomass; 2) Isolation of lignin from biomass and 3) Torrefaction process. This study was carried out at carbon capture combustion laboratory (LC₃) and biomass characterization laboratory (LCB), both belonging to energy department at FEG-UNESP.

2.1 Preparation of *in natura* biomass

In this study, sugarcane bagasse, supplied by the company Raízen, was used as raw material. They were washed with running water and allowed to immerse in water at 50 °C for 1 h in order to remove impurities such as soil residues and others contaminants, as well as non-structural sugars adhered to biomass. It was followed by drying in an oven at 100 °C for 48 h and thus grounded using the Willye-type knife mill to obtain the *in natura* biomass, named BCA.

2.2 Isolation of lignin from biomass

The chemical treatment of the BCA biomass was carried by the organosolv pulping process, at a biomass/solvent ratio of 1:10 (m/v). Acetic acid as solvent (93 % w/w), hydrochloric acid as catalyst (0.3 % w/w) and deionized water (7 %) were used in this treatment. The biomass and reagent mixture were heated to 110 °C in a round bottom flask, placed in a glycerol bath and connected to a reflux condenser with water at room temperature. After reaching the temperature, the system was kept under stirring and constant temperature for 3 h. After the treatment, the mixture was filtered, obtaining a pulp with low content of lignin as solid residue and black liquor rich in lignin as liquid residue. The biomass was then washed with deionized water until neutrality and dried in an oven for 24 h at 60 °C obtaining a delignified sugarcane bagasse, denominate BCAD.

The black liquor obtained was concentrated in a rotary evaporator at 80 °C and the lignin precipitated with the addition of deionized water in the ratio of 1:10 (v/v) and allowed to stand for 12 h. The mixture was then filtered and the solid washed with excess deionized water. As the last part of the process, it was dried in an oven at 60 °C for 24 h, to obtain the lignin (LIG).

2.3 Torrefaction process

The tests were carried out in a FORTLAB vertical tubular furnace, model FT-1200/I2, available in the combustion and carbon capture laboratory. BCA, BCAD and LIG samples were subjected to a heating rate of 10 °C/min from room temperature to 300 °C, and then maintained an isotherm for 30 min under an inert atmosphere of nitrogen at a flow rate of 100 mL/min. The obtained torrefied material of each sample was named BCA_t, BCAD_t and LIG_t.

2.4 Chemical characterization

BCA, BCAD and LIG samples were chemically characterized for the determination of lignin contents in the material, following the procedure described by the National Renewable Energy Laboratory (SLUITER et al., 2012), performing the analyzes in duplicate.

2.5 Determination of the higher heating value

The higher heating value (HHV) of the samples obtained in items 2.1, 2.2, 2.3 were determined by the Calorimeter IKA C2000, available in the Laboratory of Combustion and Carbon Capture, performing the tests in duplicate.

2.4.3 Proximate Analysis

In order to verify the volatile material (VM), fixed carbon (FC), Ashes (Ash) and moisture (M) contents present in all samples, following the procedure developed by Karatepe and Kuçukbayrak (1993). The analysis was performed by an SDT 600 thermoanalyzer (TA Instruments), using approximately 5 ± 0.5 mg of each sample.

2.5 Combustion indexes

The combustion indexes allow to evaluate the overall performance of the torrefaction process. The fuel ratio (FR) and volatile ignitability (VI) were determined using the Eq. (1) and Eq. (2), described by Conag et al. (2017):

$$FR = \frac{FC}{VM} \quad (1)$$

$$VI \text{ (MJ/kg)} = \left[\frac{HHV - 0,338FC}{VM + M} \right] \times 100 \quad (2)$$

3. RESULTS AND DISCUSSION

Table 1 presents the results obtained to HHV, percentage of lignin content in untorrified samples and proximate analysis.

Table 1. Results obtained to HHV, percentage of lignin and proximate analysis.

SAMPLE	HHV (kJ/kg)	Lignin (%)	Proximate Analysis			
			M (%)	Ash (%)	VM (%)	FC (%)
BCA	16.07	28.52	2.28	4.01	81.77	7.74
BCAD	15.05	19.22	1.72	0.37	86.18	5.00
LIG	22.32	90.00	2.13	3.89	65.14	25.14
BCAt	20.29	na	2.34	18.06	34.18	41.25
BCADt	18.57	na	1.65	8.86	68.12	16.97
LIGt	27.61	na	0.49	0	54.57	42.6

na: not applicable.

When the process for the isolation of lignin was applied to the washed biomass (BCA), it was obtained a material delignified (BCAD) with a lignin content of 19.22 %. This means that, the acetosolv pulping process removed about only 32.6 % of the lignin from the washed biomass. However, the isolated lignin (LIG) from black liquor presented a lignin content about 90 %, with a low amount of carbohydrates adhered to the material. This value is due to the fact that lignin is strongly bound to hemicellulose by means of ester bonds, and the complete cleavage of these bonds don't occur during pulping (Pinheiro et al., 2017).

When observed results of High Heating Value (HHV) from BCA, BCAD and LIG (Table 1), it was verified that the BCAD presented a lower value than the BCA, whereas the value of the LIG it was 38.9 % higher than the BCA. This behavior can be explained when it is observed the results of proximate analysis of LIG sample which is possible to notice that the value of carbon fixed (FC) is significantly higher than BCA and volatile material content (VM) is lower, obtaining the HHV value higher. In their study, Chen et al. (2018) found that lignin has higher carbon content when compared to cellulose and hemicellulose.

During the torrefaction, oxygen and hydrogen content decrease due dehydration reactions and loss of volatile organics from carbohydrate degradation, thus increasing the fixed carbon content, leading to an increase in the HHV value (Park et al., 2013; Chen et al., 2018). This could be observed in the results of torrified samples, with the LIGt presenting a HHV value of 36 % higher than the BCAt. These values can be associated to the fixed carbon content present in the sample, which follow the trend of the values found for HHV. The LIGt presented a 69 % higher HHV than LIG, showing that the torrefaction contributes significantly to increase the energy density of the material. The variation of the HHV value between the torrified and untorrified samples can be observed in Fig. 1.

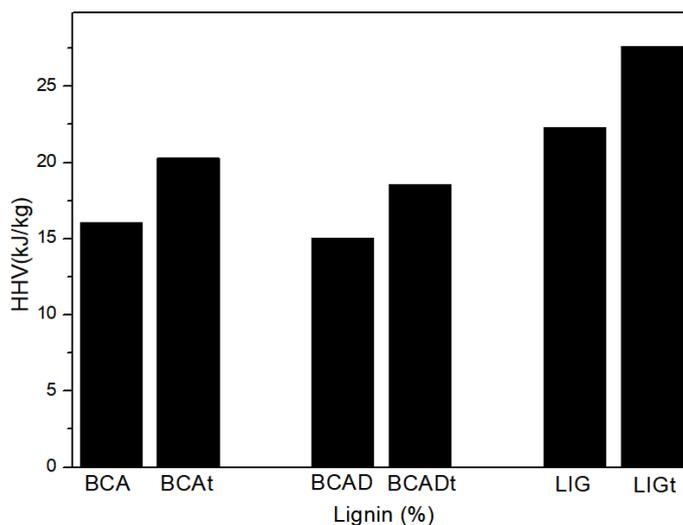


Figure 1. Variation of the HHV value between the torrefied and untorrefied samples.
 Source: the author.

In this study, it was compared the values of HHV and the lignin content of the samples as showed on Fig. 2. It is verified that the lignin content significantly influences the energy density of the sample, because with the lignin removal there was a decrease in the HHV of the biomass and its fixed carbon value.

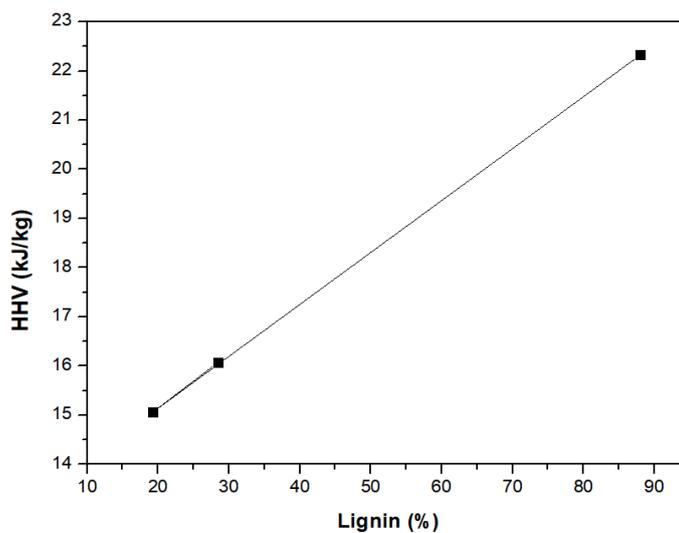


Figure 2. Relation between HHV and lignin content.
 Source: the author.

In this way the addition of lignin to the biomass could increase the energy efficiency in the torrefaction process. So, to assess the performances of torrefaction process, it was applied combustion index to the samples (BCA, BCAD, LIG, BCAt, BCADt and LIGt) using their proximate analysis. A low value for FR indicates that the material easily ignites due to the high VM content; on the other hand this high content causes incomplete combustion of the material as it is rapid and uncontrolled (Conag et al., 2017). The ideal FR values should be between 0.5 and 2.0 MJ/kg, while for VI, which indicates the available energy provided by the total volatiles, it is desired that the values exceed 14.5 MJ/kg (Conag et al., 2017).

The results are showed on Table 2. It was observed that BCAt and LIGt presented the highest FR values, indicating that these samples had a ratio of fixed carbon and volatile suitable for a combustion controlled. For VI, the highest value found was for LIGt (22.57 MJ/Kg) being about 67 % higher than BCAt. This result indicates that the torrefaction condition was more efficient when applied to LIG, because the MV content in the structure of LIG had a higher heat capacity when compared to the others samples. In addition, the FR ratio indicates that the combustion will be easily ignited.

Table 2. Results obtained to the combustion indices.

SAMPLE	FR (MJ/kg)	VI (MJ/kg)
BCA	0.15	14.33
BCAD	0.14	12.61
LIG	0.44	18.72
BCAt	1.33	13.50
BCADt	0.32	16.18
LIGt	0.82	22.57

4. CONCLUSIONS

According to the analysis of the experimental results, it was observed that the lignin contained in the biomass contributes significantly to its energy density. As it has a fixed carbon content higher than the other cellulosic constituents, it provides better HHV and VI results in the biomass.

The addition of lignin to biomass can increase the energy efficiency of the torrefaction process, since the torrefied lignin presents a fixed carbon content of 2.35 times higher than torrefied biomass, and the higher the fixed carbon value, the higher will be the value of HHV and VI.

5. ACKNOWLEDGEMENTS

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