

COB-2023-1407

PYROLYSIS OF SUGARCANE BAGASSE CHEMICALLY TREATED WITH CITRIC ACID

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Abstract. Biomass is the fourth source of energy in the world and has been found to be a potential source of renewable energy, as it can simultaneously solve the problems of energy demand and reduce GHG emissions. Among all thermochemical processes, biomass pyrolysis has the potential to produce a liquid product known as bio-oil, which has potential as a biofuel, this can minimize dependence on fossil fuels. However, the bio-oil obtained has some deficiencies such as high-water content, acidity, high content of oxygenated compounds that decrease its calorific value and, therefore, its application. To improve the yield and quality of bio-oil, the literature presents several studies on biomass pretreatment processes, where pretreatment of biomass using dilute acid solutions has generated good results, being one of the most frequently researched and applied methods. Sugarcane bagasse is a resource available in Brazil, productivity tends to increase to satisfy the demand for ethanol. Thus, more bagasse is available. Sugarcane bagasse is currently used as a fuel to produce thermal and electrical energy, however up to 18% of the bagasse is lost through bacterial decomposition. In the literature there are several works on the pyrolysis of sugarcane bagasse to produce bio-oil. The recalcitrant nature of the bagasse has an influence on the quality and yield of the bio-oil. Thus, the inclusion of a chemical treatment step before pyrolysis is interesting, as it can improve the quality and yield of bio-oil, in addition it can even reduce the temperature of pyrolysis, significantly impacting energy consumption, making the process economically more efficient. viable. In this study, the sugarcane bagasse will be chemically treated using organic acid (citric acid) and then it will be pyrolyzed at 500°C considering 30 min. Product yields and quality of products was assessed. The results demonstrate that the HHV of bio-oil obtained from the pyrolysis of chemically treated sugarcane bagasse had a significant increase.

Keywords: Sugarcane bagasse, chemical treatment, pyrolysis

1. INTRODUCTION

Worldwide, nearly 85% of energy demand is supplied by the combustion of fossil fuels such as coal, oil and natural gas. The constant use of these fuels has caused the emission of large amounts of Greenhouse Gases (GHG) into the atmosphere (Abbasi and Yozgatlıgil 2014). Of the total GHG emitted, 3/4 correspond to carbon dioxide (CO₂) which is the main anthropogenic emission responsible for global warming (Huaman and Jun 2014). According to an IPCC report (2013) there is a significant correlation between the increase in GHGs and global warming. In order to satisfy the great energy demand aiming at reducing GHG emissions, several alternatives were proposed, including the use of biomass.

Biomass is the fourth energy source in the world and has been found to be a potential renewable energy source as it can simultaneously solve energy demand problems and reduce GHG emissions (Tinwala et al., 2015; Kim et al., 2017). The use of biomass can be carried out through biochemical and thermochemical conversion processes. However, thermochemical conversion has received greater attention due to its speed and greater efficiency when compared to biochemical conversion (Tripathi et al., 2016). Among all thermochemical processes, biomass pyrolysis has the potential to produce a liquid product known as bio-oil, which has potential as a biofuel, this can minimize dependence on fossil fuels (Kabir and Hameed 2017). However, the bio-oil obtained has some deficiencies such as high-water content, acidity, high content of oxygenated compounds that reduce its calorific value and, therefore, its application (Bridgwater, 2012).

In order to improve the yield and quality of bio-oil, the literature presents several studies on biomass pretreatment processes. Due to its recalcitrant nature of lignocellulosic biomass, chemical pretreatment is one of the most important methods (Kumar et al. 2020, Kan et al. 2016). Pre-treatment of biomass with dilute acid solutions has generated good results and is one of the most frequently researched and applied methods (Rabemanolontsoa and Saka 2016; Gopalakrishnan et al. 2012).

In Brazil, sugarcane is an important source of energy, with a representation of 17.4% (base year 2017) of renewable energy sources in the Brazilian energy matrix (EPE 2018), this percentage should increase due to the improvement in its productivity and insertion of new sugarcane varieties. Thus, there is a considerable availability of sugarcane bagasse (SCB), which could be used as a raw material to produce second-generation biofuels.

The literature presents several works on SCB pyrolysis (Stegen and Kaparaju 2020; Varma and Mondal 2017; Varma and Mondal. 2016; Carrier et al. 2011; Asadullah et al. 2007) demonstrating the potential of bio-oil production, however, this product has some disadvantages such as a low quality due to the presence of oxygenated compounds, water and high pH. To improve the characteristics of SCB-derived bio-oil, recently several research have studied the influence of acid pretreatment of SCB, mainly using organic acids (Rabemanolontsoa and Saka 2016; Gopalakrishnan et al. 2012). The use of organic acids in the pre-treatment has some advantages, as they can be obtained from the biomass itself and the residues after treatment have no negative impact on the environment (Liu et al. 2015; Zhang et al 2018a; Zhang et al., 2018b). And the articles by Chia, et al. (2019) and Saad, et al. (2018) investigate the influence of process parameters such as temperature, heating rate and residence time.

However, there are few evaluated the effect of acid pretreatment of SCB using citric acid, demonstrating positive effects during the pyrolysis (Rodríguez-Machin et al. 2018; Rodríguez-Machin et al. 2019; Gomes et al. 2020). The objective of this work was to study the yields and quality of the pyrolysis products of SCB chemically treated with citric acid.

2. MATERIALS AND METHODS

Figure 1 shows the sugarcane bagasse and citric acid, for the tests it was necessary to standardize the SCB, so it underwent a grinding operation, the granulometry defined in the work was in the range of 250 - 500 μ m (Figure 1a). For chemical treatment was prepared a solution of citric acid (Figure 1b) in a concentration of 1M using distilled water



Figure 1. Materials (a) sugarcane bagasse; (b) citric acid.

Figure 2a shows a schematic of the experimental chemical treatment setup. A glass reactor with a 500ml lid will be used, where the SCB will have contact with the organic acid solution. This reactor will be on a magnetic stirrer with heating. The reactor is coupled to a condenser to prevent the escape of acidic vapors resulting from heating. A series of thermometers will allow monitoring of the process temperature. After the chemical pre-treatment has been carried out, the resulting mixture will undergo a vacuum filtering operation, separating the treated SCB from the liquid phase. After this process, the SCB resulting from each test will be washed with deionized water (to remove the remaining acid) and then dried in an oven.

Figure 2b shows a schematic of the thermal pyrolysis experimental setup. A muffle furnace with temperature control is used as heat source. The reactor has two inlets, one for the injection of carrier gas and the other for the exit of volatile material. In addition, the reactor has a thermocouple to record the internal temperature. A stream of nitrogen gas will be used to inert the medium and promote the output of volatiles, the flow will be controlled by a rotameter for nitrogen gas. A condensing system formed by a set of Liebig condensers connected in series will allow the condensation of volatile material. The condensers are connected to 2 balloons, which have the function of collecting the bio-oil. The water used by the condensing system comes from a chilled water reservoir (5°C).

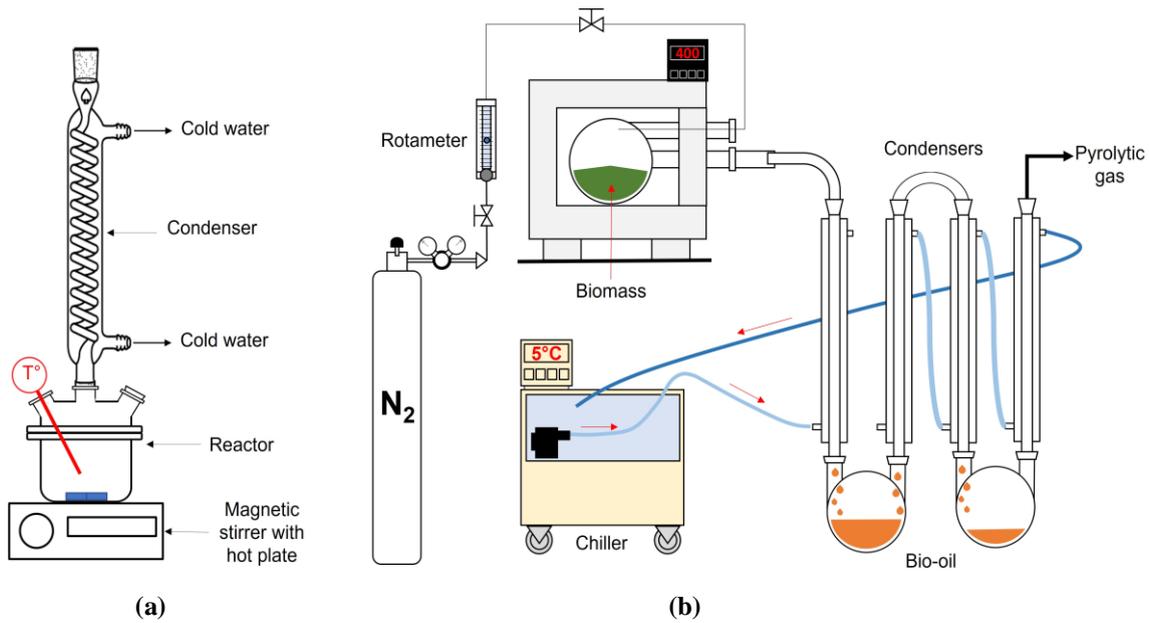


Figure 2. Experimental setups (a) chemical treatment; (b) pyrolysis unit.

The mass balance of the pyrolysis process was determined using equation 1. To determine the mass yields (MY) of the pyrolysis products, equations 2, 3 and 4 were used respectively.

$$m_{biomass} = m_{biochar} + m_{bio-oil} + m_{pyrolytic\ gas} \quad (1)$$

$$MY_{biochar} = \frac{m_{biochar}}{m_{biomass}} \quad (2)$$

$$MY_{bio-oil} = \frac{m_{bio-oil}}{m_{biomass}} \quad (3)$$

$$MY_{pyrolytic\ gas} = \frac{m_{pyrolytic\ gas}}{m_{biomass}} \quad (4)$$

Chemical treatment tests used 20g of SCB and 400 ml of 1M citric acid solution, considering a temperature of 50°C and a treatment time of 30 minutes after reaching temperature. A proportion de 1:20 g/ml between solid and liquid was suitable for the magnetic stirrer to create a homogeneous suspension (Figure 3). After treatment, SCB was filtered and washed to remove any excess citric acid. The filtering and washing stages generate a 15% loss of material.



Figure 3. SCB suspension during chemical treatment.

3. RESULTS AND DISCUSSION

Table 1 shows proximate analysis of SCA in natura and chemically treated. Using citric acid, there is a significant reduction in volatile material. The proximate analysis is the determination of fixed carbon, ash and volatile content. Which are defined by the Standards: ABNT NBR 14660 and ABNT NBR 14929, ABNT NBR 8290, TAPPI T 211 om-16 and ASTM D3172. The analysis of the volatile material content was carried out with the sample subjected to the MA 385 muffle furnace door at a temperature of approximately 950°C for 3 minutes and then placed inside the oven with the door closed for 7 minutes, ABNT NBR 8290. The ash content was carried out in accordance with the TAPPI T 211 om-16 standard, where the sample remains for 4 hours inside the muffle furnace at 600°C. The fixed carbon content was based on the ASTM D3172 Standard, which is based on the difference from other analyzes. This result can be correlated with the formation of a non-liquid base due to the extraction of some water from the SCB structure. The results show that citric acid has a high effect due to the number of carboxylic group (COOH) that has 3 groups, this was also pointed out in the work of Rodriguez-Machin et al. (2018) and Rodríguez-Machin et al. (2019). It's noted that HHV will decrease a few, according to Gomes et al. (2020) this may be due to partial decomposition of the biomass structure, mainly hemicellulose and a small fraction of cellulose.

Table 1. Proximate analysis of SCB and SCB chemically treated.

Property Dry basis (%)	SCB	SCB chemically treated
Volatile material	85,48	75,3
Fixed carbon	11,56	22,3
Ash	2,94	2,4
HHV (MJ/kg)	15,80	15,38

Table 2 shows the mass yields obtained in the pyrolysis of bagasse and treated bagasse. It can be observed that in the pyrolysis of treated sugarcane bagasse there is a significant reduction in the yield of biochar, but an increase in the yield of bio-oil and even more so of the pyrolytic gas. Rodríguez-Machin et al. (2019) have reported a similar behavior. This indicates that the chemical treatment facilitated the thermal decomposition of the sugarcane bagasse.

Table 2. Yield of products obtained by pyrolysis.

Mass yield (%)	SCB	SCB chemically treated
Biochar	35	24,8
Bio-oil	40	43,2
Pyrolytic gas	25	32,0

Figure 4 shows the products collected from the pyrolysis of sugar cane bagasse. Figure 4a shows biochar, which does not exhibit differences due to the chemical treatment of sugarcane bagasse. However, in the case of bio-oil, qualitative differences are already observed. Figure 4b shows the bio-oil obtained from the pyrolysis of SCB without treatment. On Figure 4b, the bio-oil has a lighter brown color, where you can see the aqueous part and a dark dense phase dispersed on the wall and bottom of the tube. Figure 4c shows the bio-oil obtained from the pyrolysis of SCB chemically treated, which exhibits a much darker color. Bio-oil does not exhibit phase formation, it is more homogeneous.

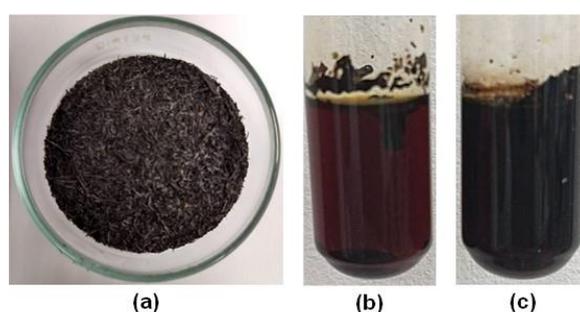


Figure 4. Pyrolysis products (a) biochar; (b) bio-oil from SCB; (c) bio-oil from SCB chemically treated.

Table 3 exhibit the HHV of bio-oil. The bio-oil from SCB chemically treated have a higher value of HHV when compared with the bio-oil from the pyrolysis of SCB without treatment. According to Gomes et al. (2020), the chemical treatment of SCB can reduce the hemicellulose content. Thus, the pyrolysis of SCB chemically treated has a higher cellulose content, due to the decomposition of a significant fraction of the hemicellulose. Cellulose is the main component of biomass, which during its pyrolysis ends up being largely the mass yield of bio-oil.

Table 3. HHV of bio-oil.

Bio-oil - SCB (MJ/kg)	Bio-oil – SCB treated (MJ/kg)
6,10	10,70

Table 4 presents the results of the immediate analysis of biochar from SCB and biochar from SCB chemical treatment. All samples were previously dried to avoid interference with the reading of other variables. The results demonstrate that biochar exhibits a reduction in volatile material content when sugarcane bagasse is treated with citric acid. It is also observed that the fixed carbon content increases, promoting an increase in the HHV of the biochar. The ash content exhibits a reduction, this can be explained due to the leaching effect of the citric acid solution, which may have removed the inorganic elements from the structure of the biomass particle, this behavior was appointed on Rodríguez-Machin et al. (2018).

Table 4. Proximal analysis of biochar.

Property Dry basis (%)	SCB	SCB chemically treated
Volatile material	41,21	34,0
Fixed carbon	43,66	52,1
Ash	15,13	13,9
HHV (MJ/kg)	27,41	31,7

4. CONCLUSIONS

The chemical treatment of SCB demonstrates a significant effect on bio-oil composition. The pyrolysis of SCB chemically treated has a different behavior due to changes in compositional structure. Bio-oil obtained by pyrolysis of SCB chemically treated has a HHV higher than bio-oil without treatment. Chemical treatment facilitates thermal decomposition of biomass. Biochar from SCB chemically treated has a higher calorific value due to the removal of part of the ash content.

5. ACKNOWLEDGEMENTS

The authors would like to thank the Higher Education Personnel (CAPES), National Council for Scientific and Technological Development (CNPq) (Process – 406810/2022-2).

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