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IN-SITU CATALYTIC PYROLYSIS OF SUGARCANE BAGASSE USING CALCIUM CARBONATE FOR BIOFUEL PRODUCTION

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Abstract. *Currently, to satisfy energy demand aiming at reducing greenhouse gas emissions, mainly carbon dioxide (CO2), the use of biomass has been proposed. Brazil is a major producer of sugarcane and generates a large amount of sugarcane bagasse (SCB). The biomass pyrolysis process has been studied as a process with the potential to produce biofuels (bio-oil, biochar and gas) with high energy density, however the bio-oil obtained from the thermal pyrolysis process has a high oxygen content, which impairs the quality and calorific value of the bio-oil. This problem can be solved with the addition of a catalyst. In this work, CaCO3 was used as a catalyst in the pyrolysis of SCB and demonstrated that the catalyst influences the pyrolysis products. The presence of the catalyst caused a significant increase in the mass yield of the biochar, however, keeping the yields of bio-oil above 40%, the mass yield of the pyrolytic gas was below 20%. In the bio-oil obtained with the presence of the catalyst, a color clarification was observed, which indicates a clear change in the chemical composition. The calorific value of the biochar obtained in the thermal condition is superior to the catalytic one.*

Keywords: *Biomass, sugarcane bagasse, bio-oil, calcium carbonate, catalytic pyrolysis.*

1. INTRODUCTION

Currently, in order to satisfy the great demand for energy in order to reduce greenhouse gas (GHG) emissions, mainly carbon dioxide (CO2), several alternatives have been proposed, including the use of biomass. In the world, biomass is the fourth energy source and has been identified as a renewable energy source capable of solving energy demand problems and reducing GHG emissions (Saidur et al., 2011; Tinwala et al., 2015). ; Kim et al., 2017). Lignocellulosic biomasses are polymer units that contain hemicellulose (15-25%) in their composition; cellulose (40-50%) and approximately (15-35%) of lignin (Cao et al., 2020). Brazil has an energy matrix in which sugarcane has a share of 18% (base year 2019) (EPE 2020), this percentage should increase due to the improvement in its productivity. According to CONAB 2019, the estimated sugarcane production for the 2019/20 harvest is 615.98 million tons, considering that the crushing of 1 ton of cane generates approximately 250 kg of bagasse, there would be an availability of 153.99 million tons of sugarcane bagasse.

The use of biomass can be carried out through biochemical and thermochemical conversion processes. However, thermochemical conversion has received more attention due to its speed and greater efficiency when compared to biochemical conversion (Tripathi et al., 2016). Among thermochemical conversion processes, pyrolysis has the potential to produce energy-dense biofuels from non-food resource sources (agricultural, urban, industrial and animal waste) (Demiral and Sensöz 2006). According to Kabir and Hameed (2017), the pyrolysis of lignocellulosic biomass not only produces renewable fuels, but also products derived from petroleum; consequently this can minimize dependence on fossil fuels. Pyrolysis is the process of thermal decomposition in an inert medium that results in three products: a solid (biochar), a liquid (bio-oil) and a gas (pyrolytic gas) (Demiral and Sensöz 2006; Tripathi et al., 2016).

Biomass pyrolysis has several types, the most studied being fast pyrolysis and slow pyrolysis, the latter being mainly oriented towards the production of biochar (Russell et al., 2017). The production of bio-oil, from the process of thermal pyrolysis, has a high content of oxygen, which impairs the quality and calorific value of bio-oil. Studies show that catalytic pyrolysis, using an alkaline catalyst or basic metal oxides, favors the deoxygenation reaction of bio-oil, thus increasing its quality (Charusiri and Vitidsantb 2017).

The literature presents some works on catalytic pyrolysis of biomass, several studies show that catalytic pyrolysis has a positive effect on products, mainly on the quality of bio-oil (Charusiri and Vitidsantb 2017; Case et al., 2015; Cao et al., 2020; Chen et al., 2019; Chireshe et al., 2020). The catalyst in catalytic pyrolysis can be mixed directly into the IN-SITU biomass, or placed in a separate reactor from the biomass, with contact with volatiles, EX SITU. Some of the advantages of in situ catalytic pyrolysis are the low cost and the easier assembly process (Dutta et al., 2015). Cao et al., (2020) studied catalytic pyrolysis of rice straw using basic metallic oxides as a catalyst at temperatures of 300, 400, 450 and 500°C in an inert medium, 10g of dry biomass, with 10% of CaO, MgO and CaCO3 with heating rate 10 °C/min with 1h. The highest bio-oil yield was obtained with MgO, the percentage of biochar was higher with the CaO catalyst, while in the presence of CaCO3 there was a high production of pyrolytic gas (27.5%). The main objective of this study is to analyze the influence of CaCO3 as a catalyst in the yields and quality of products, mainly bio-oil and biochar, from the IN-SITU catalytic pyrolysis of sugarcane bagasse.

2. MATERIALS AND METHODS

2.1 Materials

Figure 1(a) shows the sugarcane bagasse (SCB). For the experiment, milled sugarcane bagasse was used in a granulometry of 250-500um. This granulometry was chosen to obtain a more homogeneous mixture with the catalyst. The mass was 20g. Figure (b) shows the catalyst used calcium carbonate - CaCO3.

Figure 1. (a) Sugarcane bagasse; (b) Calcium carbonate.

2.2 Experimental pyrolysis bench

Figure 2 shows the experimental bench used in the thermal and catalytic pyrolysis experiments. The energy required for heating the biomass was obtained through the muffle furnace. The volumetric flow rate of N2 gas was 100 ml/min measured by a rotameter to create an inert environment inside the reactor. Two condensers were used through which chilled water circulated at a constant temperature of 5 °C to condense the condensable fraction of volatiles and thus obtain the bio-oil. The temperatures evaluated were 300, 400 and 500 °C, considering a constant time of 30 minutes once the process temperature has been reached. The percentage of catalyst was 10% by mass, which was previously mixed with the biomass and then fed into the reactor.

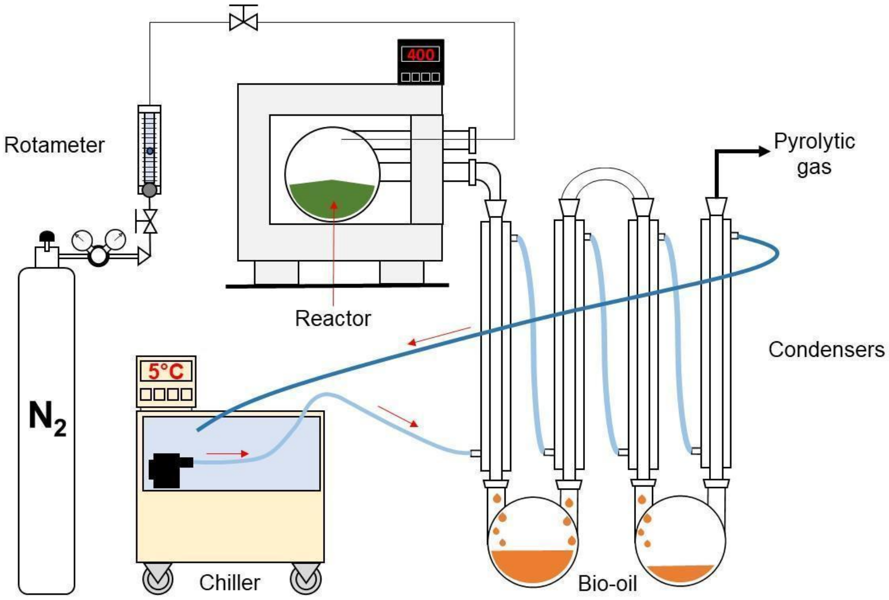

Figure 2. Experimental setup for biomass pyrolysis.

2.3 Pyrolysis evaluation parameters

Yields were calculated with the following Equations.

$$\text{Bio-oil} = \frac{\text{Mass of Bio-oil} * 100}{\text{Biomass Mass}} \tag{1}$$

$$\text{Biochar} = \frac{\text{Mass of Biochar} * 100}{\text{Biomass Mass}} \tag{2}$$

$$\text{Pyrolytic gas} = \text{final } M \text{ bio-oil} + \text{final } M \text{ biochar} + \text{final } M \text{ pyrolytic gas} = 100\% \tag{3}$$

2.4 Characterization techniques

In this part, the techniques used in the characterization of sugarcane bagasse are demonstrated. Compositional analysis was applied to determine the amounts of hemicellulose, cellulose and lignin, which followed the TAPPI standard procedure. Immediate analysis was used to determine moisture, volatiles, ash and fixed carbon. The pH meter (AK 151) was used to determine the pH in the bio-oil. The IKA C500 calorimeter was used to determine the calorific value of biochar and bio-oil thermal and catalytic pyrolysis products. All assays were performed in triplicate.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of sugarcane bagasse

Observing Table 1, it is possible to verify a high cellulose content (41.64%), and the other components are within the literature range. What may have caused this variation in levels is the place of cultivation and the harvest of the biomass. When there is a higher concentration of cellulose and hemicellulose, it implies a greater amount of the liquid fraction (bio-oil), and when high concentrations of lignin are obtained, the production of the solid product (biochar) is favorable. Immediate analysis is used to explore the combustion properties and quality of bagasse as biomass. The moisture content found for SCB is 5.5%, which is close to the values found in the literature. The moisture of the biomass can lead to a large generation of acid extract, which causes a decrease in the calorific value of the bio-oil. Thus, the process may become infeasible as it would require more energy and time (SILVA, 2013). The contents of fixed carbon and volatile material are within the studied literature. It is observed that there is a large percentage of volatile material, in which the production of bio-oil and gasses through pyrolysis becomes viable, being derivatives of cellulose and hemicellulose. Fixed carbon influences the production of biochar, where it is derived from lignin. The ash content obtained is also in accordance with the limits of the literature presented. In order to carry out pyrolysis aiming at the production of bio-oil, it is interesting that this content is low, as it can cause energy loss and reduce the conversion rate of the process, in addition to forming incrustations, slag and corroding the interior of the reactor.

Table 1. Chemical composition and imediate analysis of SCB

Characteristics	**In this study**	**Varma and Mondal (2017)**
Composition	%	
Cellulose	41,64	47,60
hemicellulose	29,74	39,00
lignin	22,86	11,20
Extractives	6,49	2,20
Immediate analysis		
Moisture	5,5	5,40
Volatile Material	80,8	80,20
fixed carbon	11,2	11,30
ashes	2,5	3,10

3.2 Pyrolysis yield

Figure 4 shows the yields of the thermal pyrolysis products of SCB at the temperatures studied. It can be seen that the bio-oil yield is higher at all temperatures studied, always being above 40%. The biochar yield was greater than 20% under all conditions, however the highest yield was obtained at 300°C. It is observed that the biochar yield decreases with increasing temperature, due to a greater thermal decomposition of the biomass. The pyrolytic gas yield increased proportionally with temperature, reaching a maximum at 400°C and a slight reduction at 500°C.

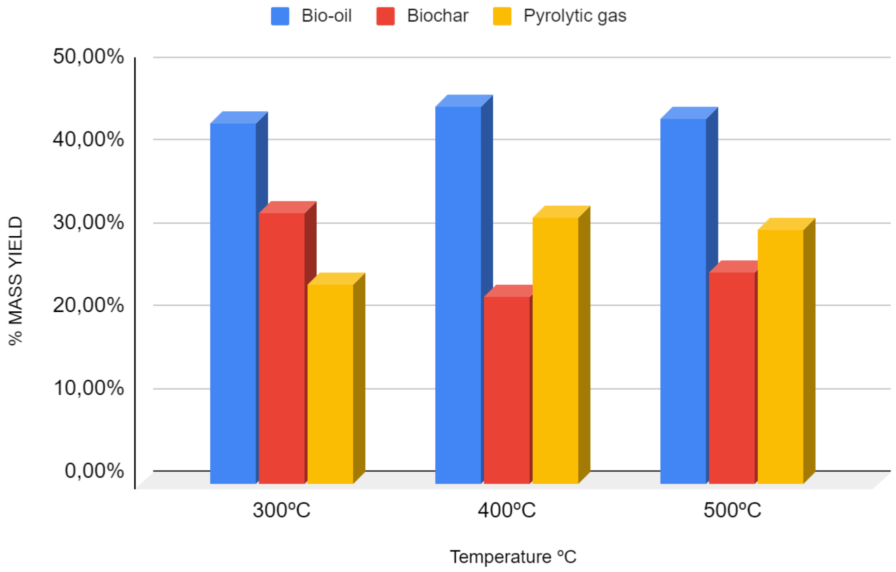

Figure 4. Thermal pyrolysis yields.

Figure 5 shows the mass yields of IN-SITU catalytic pyrolysis of SCB. The yields shown do not consider the mass of the catalyst. The presence of the catalyst caused a significant increase in the mass yield of the biochar, but keeping the bio-oil yields above 40%. The mass yield of pyrolytic gas is below 20%, the lowest being obtained at 300°C and the highest at 500°C. The results confirm that the presence of the catalyst promotes an increase in the production of biochar.

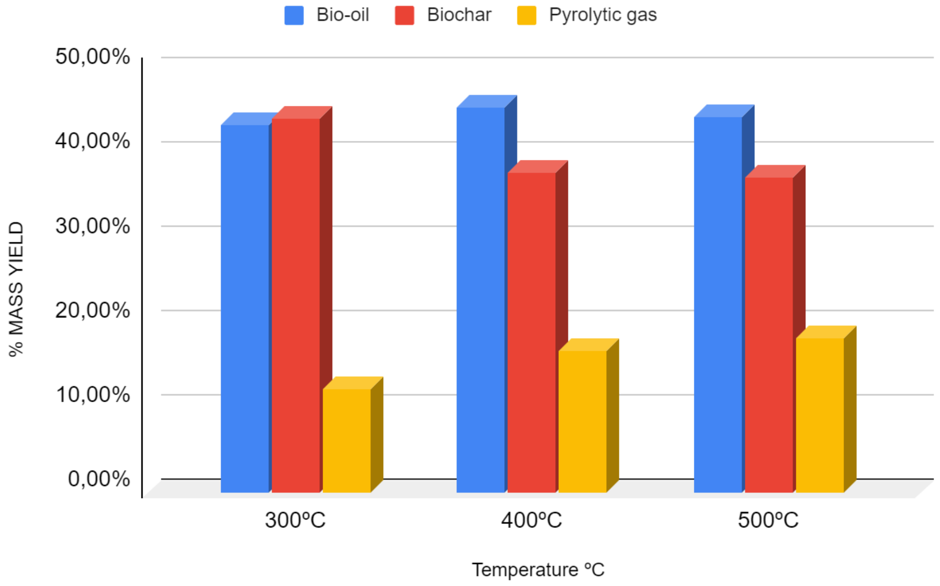

Figure 5. IN-SITU Catalytic pyrolysis yields.

3.3 Characterization of pyrolysis products

Figure 6 shows samples of the biochar obtained from the IN-SITU thermal and catalytic pyrolysis of SCB. The biochar obtained in the thermal pyrolysis does not show significant differences, with all samples being black. However, the biochar obtained from IN-SITU catalytic pyrolysis exhibits significant differences, the biochar obtained at 300°C exhibits a gray color due to the mixture between the biochar and the catalyst, but as the temperature increases, the biochar becomes darker.

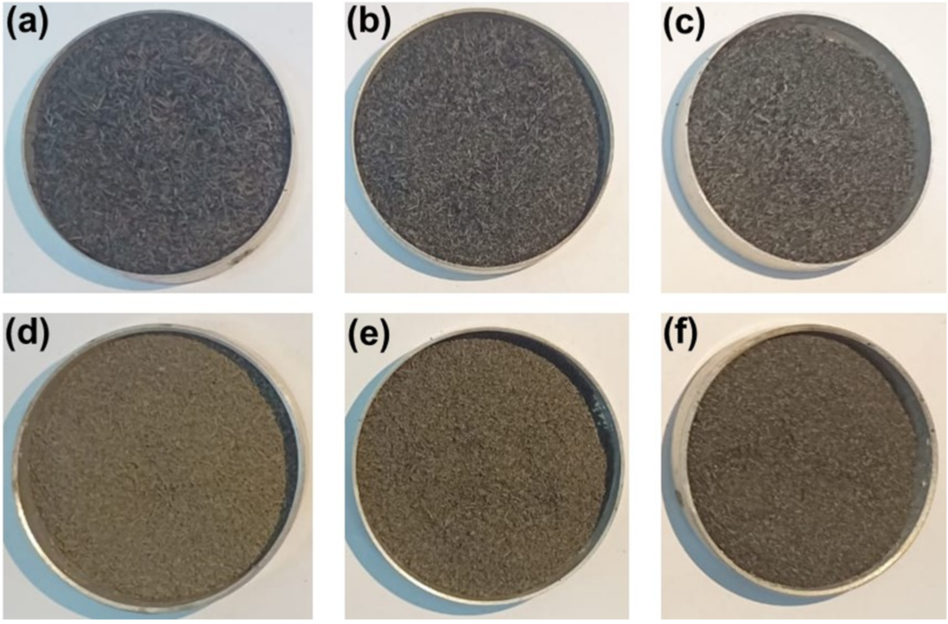

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Figure 6. In-SITU catalytic pyrolysis yields of SCB biochar (a) thermal 300°C (b) thermal 400°C (c) thermal 500°C (d) catalytic pyrolysis 300°C (e) catalytic pyrolysis 400°C (f) catalytic pyrolysis 500°C.

Figure 7 shows the bio-oils obtained from the thermal and catalytic pyrolysis of SCB. Under all conditions, the catalyst used observed a similar color of the bio-oil. In addition, a strong odor indicative of volatile products (smell similar to acetone) was noted. Figures 7a and 7b represents the bio-oil without and with the use of catalyst, regardless of temperature (500°C), it presented the same qualitative characteristics (smell). Figure 7c shows the dense fraction of the bio-oil obtained in the thermal condition, which exhibits a greater amount of material when compared to the dense fraction of the bio-oil obtained in the catalytic condition (Fig 7d). The difference may be that in the catalytic condition there are cracking reactions of the organic substances present in the bio-oil.

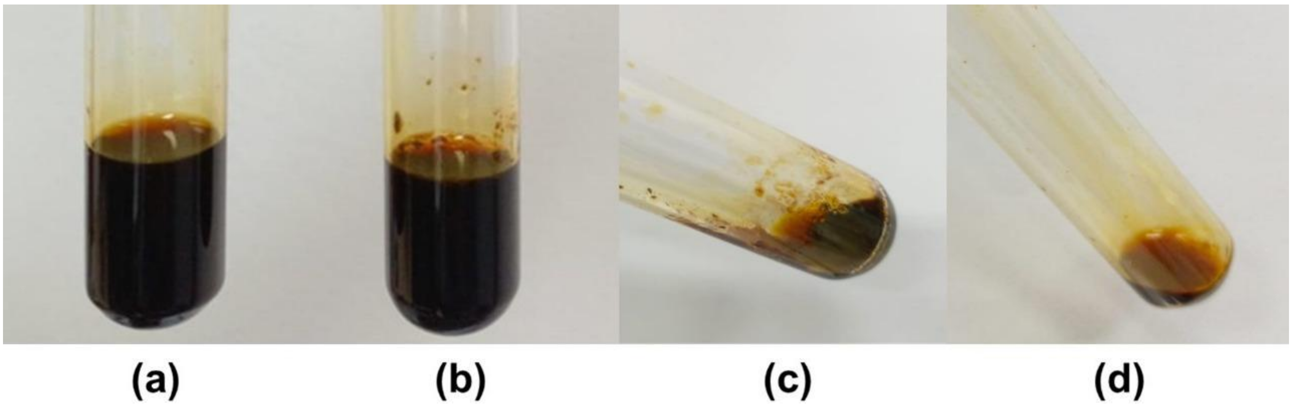

Figure 7. SCB bio-oil (a) without catalyst (b) with catalyst (c) denser fraction without catalyst (d) denser fraction with catalyst.

Table 5 displays the values of the higher calorific value of the biochar obtained under thermal and catalytic conditions. The results demonstrate that the values of the calorific value obtained in the thermal condition are superior to the catalytic ones. This is due to the presence of the catalyst, which increases the mass fraction of inorganic substances, thus significantly reducing the calorific value. Thus, the biochar obtained in the catalytic condition would not be suitable for use as solid fuel, although the use of biochar from catalytic pyrolysis in situ as a solid fuel is not recommended, this biochar can be used for other applications such as biochar-concrete composites (Akhtar and Sarmah 2018).

Table 5. PCS (MJ/kg) of biochar samples.

Condition	300°C	400°C	500°C
thermal	25,70	22,30	23,18
catalytic	17,21	17,51	16,89

Table 6 presents the values of the calorific value of the bio-oil obtained through the conditions of thermal and catalytic pyrolysis processes. The results demonstrate that the values of calorific value obtained in the catalytic condition are superior, approximately twice, in relation to those obtained in the thermal condition. This may be due to the reaction between calcium and volatile material released during the process. It is also observed that the highest calorific value is found in the catalytic sample at 500ºC, this may be due to the increase in the effective thermal decomposition of lignin. However, it is observed that in the catalytic condition between 300°C and 500°C, the calorific value of the bio-oil does not present many differences, thus demonstrating the possibility of producing a cheaper bio-oil due to a lower energy demand in the process. of pyrolysis.

Table 6. PCS (MJ/kg) of bio oil samples.

Condition	300°C	400°C	500°C
thermal	7,05	8,82	8,05
catalytic	17,72	16,92	18,62

4. CONCLUSION

It was observed that the use of calcium carbonate ($CaCO_3$) in the in situ catalytic pyrolysis of SCB managed to preserve the mass yield of bio-oil in relation to the thermal pyrolysis of SCB, there was a significant increase in the mass yield of biochar and the reduction in yield of pyrolytic gas. In the liquid part, it was visually observed a clarification of the bio-oil obtained with the use of $CaCO_3$ in relation to the thermal condition. From the energy point of view of the biochar, it was observed that the calorific value of the catalytic condition is lower in relation to the thermal condition, so the biochar of the catalytic condition is not suitable for energy application, but other applications could be evaluated as examples: fertilizers, corrector of soil, catalyst among others.

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